## TASK 2 IMPAIRMENT ASSESSMENT REPORT FOR COPPER AND NICKEL IN LOWER SOUTH SAN FRANCISCO BAY



Final Report - June 2000

Prepared by

TETRA TECH, INC.

ROSS & ASSOCIATES

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#### Acknowledgments

The Impairment Assessment Report for Copper and Nickel in Lower South San Francisco Bay is the product of co-operative efforts by several groups. Funding was provided by the City of San Jose's Environmental Services Department. Guidance for the impairment assessment was provided by the Copper and Nickel TMDL Work Group. This group was formed by the Santa Clara Basin Watershed Management Initiative, and participants include representatives from regulatory and resource agencies, environmental advocacy groups, industry, and municipalities. The TMDL Work Group oversaw the selection of indicators and the development of endpoints that were used to assess beneficial-use impairment, reviewed draft reports, and approved the final report. In the review process, a Technical Review Committee was formed to provide expert review of the impairment assessment. Members of the Technical Review Committee were Dr. Jim Kuwabara from the U.S. Geological Survey, Dr. Ken Bruland from University of California, Santa Cruz, Mr. David Hansen from HydroQual, Inc., and Dr. Jonathan Phinney from the Center for Marine Conservation. Their recommendations were incorporated into this report. The impairment assessment report was prepared by Tetra Tech, Inc., Eisenberg, Olivieri & Associates, Inc., and Ross & Associates Environmental Consulting, Ltd.

This report was prepared under Task 2 of the project entitled: Calculation of Total Maximum Daily Loads for Copper and Nickel in Lower South San Francisco Bay. Two additional reports were produced under this project that were crucial to the impairment assessment: Source Characterization Report and the Conceptual Model Report. Together these three reports were used to assess the need to complete the TMDL.

The TMDL Work Group is in general agreement with the use of existing information in this report to assess the existence and maintenance of beneficial uses of Lower South San Francisco Bay, and the TMDL Work Group formally accepts the three key findings of this report:

- Impairment of beneficial uses due to copper and nickel is unlikely
- The ranges of proposed site specific objectives for copper and nickel are scientifically defensible
- Uncertainties regarding the scientific information remain

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Prepared by:

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June 2000

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#### **Glossary of Terms**

Acute toxicity bioassay endpoints are expressed as either, a) an estimate of the toxicant concentration which is lethal to 50% of the test organisms in the time period prescribed by the test. This is expressed as the LC50, or b) the highest toxicant concentration at which survival is not significantly different from the control (No-Observed-Adverse-Effect Concentration, or NOAEC) (USEPA 1991).

The Criteria Maximum Concentration (CMC) is the highest allowable concentration of a pollutant to which aquatic life can be exposed for a short period of time (generally < 1 hour). The CMC is equal to one-half the Final Acute Value and is intended to protect 95% of a group of diverse genera, unless a commercially or recreationally important species is very sensitive. However, a concentration that would severely harm 50 percent of the fifth percentile or 50 percent of a sensitive important species cannot be considered to be protective of that percentile or that species. Dividing the Final Acute Value by 2 is intended to result in a concentration that will not severely adversely affect too many of the organisms (Stephan, et al., 1985).

The purpose of chronic toxicity bioassay tests is to estimate the highest concentration of a toxicant which produces no measurable, significant effect (no-effect concentration). These endpoints are generally limited to hatch success, gross morphological abnormalities, survival, growth, and reproduction. The results are generally presented as the highest concentration of a toxicant that has no statistically significant observed effect on these responses, when compared to the controls.

The Criteria Continuous Concentration (CCC) is the highest concentration of a pollutant that can be continuously maintained in a water body without unacceptably affecting aquatic organisms or beneficial uses (U.S. EPA 1997). The CCC is intended to be a good estimate of the threshold of unacceptable effect (Stephan, et al. 1985).

The common endpoints are:

- No-Observed-Effect Concentration (NOEC) is the highest concentration of a toxicant
  to which organisms are exposed in a full life-cycle or partial life-cycle (short-term) test
  that causes no observable adverse effects on the test organism (i.e., where the values
  for the observed responses are not significantly different from those observed in the
  controls).
- Lowest-Observed-Effect-Concentration (LOEC) = The lowest concentration of a toxicant to which organisms are exposed in a full life-cycle or partial life-cycle (short-term) test, which causes adverse effects on the test organism (i.e., where the values for the observed response are significantly different from those observed in the controls).
- Effect Concentration (EC) = A point estimate of the toxicant concentration that would cause an observable adverse effect on the quantal (all or nothing) response (e.g., death, immobilization, or serious incapacitation) in a given percent of the organisms. If the observed effect is death or immobility, the term Lethal Concentration (LC), should be used. A certain EC or LC value might be judged from a biological standpoint to represent a threshold concentration, or lowest concentration that would cause an adverse effect on the observed response.

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- Inhibition Concentration (IC) = The toxicant concentration that would cause a given percent reduction in a non-quantal biological measurement for the test population. For example the IC25 is the concentration of toxicant that would cause a 25% reduction in mean young per female or in growth for the test population, and the IC50 is the concentration of toxicant which would cause a 50% reduction (USEPA 1994). IC25 and EC25 are used for chronic toxicity monitoring endpoints in this region.
- **Geometric Mean** is calculated by summing the logarithms of N numbers, dividing the sum by N, and taking the anti-log of that quotient.
- Species Mean Acute Value (SMAV) is the geometric mean of the acute responses that
  were exhibited by organisms of the same species, using the same toxicant and dilution
  water.
- **Genus Mean Acute Value (GMAV)** is the geometric mean of the SMAV that are within the same genus.
- **Final Acute Value (FAV)** is the result of performing a modified regression analysis on the 4 GMAVs which have cumulative probabilities closest to 0.05. This makes the Final Acute Value an estimate of the concentration of a pollutant that is protective of 95% of the genera represented in the data-set.
- Species Mean Chronic Value (SMCV) is the geometric mean of the chronic that were exhibited by organisms of the same species, using the same toxicant and dilution water.
- **Final Acute-to-Chronic Ratio (FACR)** is a way of relating acute and chronic toxicities of pollutants to aquatic organisms. It is calculated by using the quotient of the Species Mean Acute Values as the numerator and the Species Mean Chronic value as the denominator

$$SMAV \div SMCV = FACR$$

Only like tests can be used to calculate this ratio (e.g., same species, water, and measured pollutant concentrations).

• **Final Chronic Value (FCV)** is the quotient of the Final Acute Value and the Final Acute-to-Chronic Ratio,

• Criterion Maximum Concentration (CMC) is the highest allowable concentration of a pollutant to which aquatic life can be exposed for a **short** period of time (e.g., 1-hour) and is calculated by dividing the Final Acute Value by 2,

$$FAV \div 2 = CMC$$
.

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- Criterion Continuous Concentration (CCC) is the highest concentration of a pollutant that can be continuously maintained in a water body without unacceptably affecting aquatic organisms or beneficial uses. The CCC is often equal to the Final Chronic Value.
- Site-Specific Criterion Requirements Before any water quality criterion can be calculated, certain requirements must be met. These requirements ensure that a broad base of aquatic organisms is included in any data-set used to calculate a criterion, whether it be national or site-specific.

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#### **ADDENDUM**

One of the most important uncertainties identified in the impairment assessment was the toxicity of copper to phytoplankton. In the Draft Final Impairment Assessment Report this information on copper toxicity to phytoplankton was summarized in the following statement: "Several studies have reported on the sensitivity of several classes of phytoplankton (cyanobacteria, coccolithophores, dinoflagellates, and diatoms) to free ionic copper. These classes of phytoplabnkton were found to exhibit reduced growth at free ionic copper concentrations as low as approximately 10<sup>-11</sup> M with cyanobacteria being the most sensitive to free ionic copper concentrations followed in order of decreasing sensitivity by coccolithophores, dinoflagellates, and diatoms." The Technical Review Committee that reviewed the draft final version of this report recommended special studies to determine whether cyanobacteria growth is impaired in Lower South San Francisco Bay.

Additional information has recently become available regarding the occurrence of the cyanobacteria *Synechococcus* sp. in San Francisco Bay. Two papers<sup>1</sup> included in Appendix I of this report show that cyanobacteria were a "persistent component of the San Francisco Bay phytoplankton in all the estuarine habitats" in 1998 and 1999. In light of this new information, the TMDL Work Group requested the Technical Review Committee to examine this new information and to comment on its significance to findings of the impairment assessment. Their review is summarized in Appendix H. The Technical Review Committee's responses to specific questions regarding the significance of the new information on the occurrence of cyanobacteria in Lower South San Francisco Bay lend support to the overall finding that impairment to the beneficial uses due to ambient copper concentrations is unlikely.

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<sup>&</sup>lt;sup>1</sup> Ning, X., J. E. Cloern and B. E. Cole. 2000. Spatial and temporal variability of picocyanobacteria *Synechococcus* sp. in San Francisco Bay. Limnol. Oceanogr. (in press); Palenik, B. and A. R. Flegal,1999. Cyanobacterial populations in San Francisco Bay. Regional Monitoring Program for Trace Substances, Technical Report. (http://www.sfei.org/rmp/reports/cyanobacterial.html)

#### **EXECUTIVE SUMMARY**

This report presents the beneficial use impairment assessment for copper and nickel that was developed as a part of the Total Maximum Daily Loads (TMDL) project for Lower South San Francisco Bay. The purpose of this report is to present new information and to re-evaluate the determination that the beneficial uses of the Lower South San Francisco Bay are impaired due to ambient concentrations of copper and nickel. This impairment assessment was conducted to provide the information necessary to help stakeholders evaluate whether or not beneficial uses are currently being impaired in Lower South San Francisco Bay. A five-step strategy was used:

- 1. Compile and evaluate data on ambient concentrations and toxicity information for copper and nickel in the Lower South San Francisco Bay
- 2. Identify, evaluate and select indicators of beneficial-use impairment
- Develop endpoints for the selected indicators that can be used to assess the existence of impairment and compare these values to ambient concentrations in Lower South San Francisco Bay
- 4. Assess the level of certainty required to determine whether ambient concentrations of copper and nickel are or are not resulting in beneficial-use impairment
- 5. Evaluate numeric values for site-specific objectives for dissolved copper and nickel in Lower South San Francisco Bay

The impairment assessment relies on a "weight of evidence" approach. All available evidence was reviewed and incorporated in proportion to its applicability, technical certainty, and statistical validity in evaluating the likely impacts and impairment of beneficial uses. The following potential conclusions and outcomes to the beneficial use impairment assessment were considered as part of developing the impairment assessment findings:

- **No impairment**: The lines of evidence and indicators unequivocally demonstrate no negative impact to Beneficial Uses due to copper and nickel.
- **Impairment unlikely**: The evidence clearly support the judgement that copper and nickel are not causing a negative impact to Beneficial Uses. This level of finding includes some uncertainty.
- **Possible impairment**: The evidence suggests the existence of diminished ecosystem integrity that causes a negative impact on a designated Beneficial Use from copper or nickel. There are uncertainties associated with this finding that must be addressed with additional studies designed to confirm the existence and/or level of impairment.
- **Definite impairment**: The evidence clearly indicates a negative impact on designated Beneficial Uses due specifically to ambient concentrations of copper and nickel. There are substantial documented data to support the finding, and there are few if any uncertainties associated with the assessment conclusion.

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• Cannot determine impairment: This finding does not indicate impairment or non-impairment of the designated Beneficial Uses. The uncertainties are due to 1) inadequate data, 2) lack of knowledge regarding basic processes, or 3) status of resident aquatic life and wildlife populations.

#### Ambient Conditions in Lower South San Francisco Bay

The prescribed impairment assessment strategy required an adequate characterization of existing water quality and ecological conditions, as well as access to an extensive toxicity database. This Impairment Assessment used an unprecedented number of data to determine the effects of copper and nickel on the beneficial uses. Over 3,100 measurements of both total and dissolved copper and nickel were compiled from more than 20 locations within the Lower South San Francisco Bay. In addition, water column and sediment toxicity data were compiled from four separate studies performed in the Lower South San Francisco Bay over the last ten years.

Identify, Evaluate, and Select Indicators

A technical workshop was held in January 1999 to describe candidate indicators and their use in the impairment assessment process. Based on information presented at this workshop, a primary set of seven indicators were defined and considered for inclusion in the impairment assessment: Individual Species Toxicity Tests, Aquatic Ecological Risk Assessment Protocol (AERAP), Site-Specific Studies, Phytoplankton, Simultaneously Extracted Metals/Acid Volatile Sulfides, Benthic Macroinvertebrates, and Charismatic Macrofauna (harbor seals and birds). Each indicator was evaluated, and those that met the requirements of the Indicator Evaluation Criteria were selected for use in the Impairment Assessment. Four of the seven potential indicators were selected:

Individual Species Toxicity Tests Indicator – This indicator used the toxicological responses of aquatic organisms to a selected stressor (e.g., copper or nickel) as an indicator of potential environmental impairment. These responses were obtained from peer-reviewed published sources, where the tests were performed using single stressors under controlled laboratory conditions and water that contained little or no metal complexing capacity. The results of this indicator were considered to be highly conservative and formed the base from which local site-specific water quality objectives could be determined.

AERAP Indicator – This risk-based methodology was used to assess the effects of toxicants at the community level. Four different subsets of the national toxicity database were used in this analyses: 1) the national dataset (complete set), 2) Resident/Surrogate dataset (those species that were either residents of South San Francisco Bay or commonly used as surrogate test organisms), 3) the U.S. EPA "WER Cookbook" species deletion dataset (a subset of the national dataset that remained after the deletion rules had been followed), and 4) the Resident dataset (species resident to the Lower South San Francisco Bay).

*Site-Specific Studies Indicator* – This indicator used the results obtained from toxicity tests conducted using ambient Lower South San Francisco Bay water and resident species to provide an estimate of the amount of copper and nickel that is bioavailable. This allowed for a site-

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specific water quality objective that was fully, yet not overly, protective of the beneficial uses of Lower South San Francisco Bay. The results of the site-specific studies were used to determine whether existing national water quality criteria were over-protective of the beneficial uses, and therefore, inappropriate for Lower South San Francisco Bay.

**Phytoplankton Indicator** - The use of phytoplankton as an indicator of beneficial-use impairment in Lower South San Francisco Bay was specifically evaluated for several reasons. Phytoplankton are an essential part of the food chain that supports all ecological beneficial uses of the Lower South Bay. Phytoplankton also play an essential role in the biogeochemical cycling of copper and nickel. Additionally, a notable body of scientific evidence indicated that phytoplankton (*i.e.*, cyanobacteria, coccolithophores, dinoflagellates, and diatoms) were sensitive to very low concentrations of free ionic copper in marine and estuarine systems.

#### **Development of Indicator Endpoints**

Multiple measurement endpoints were used in the assessment. The Individual Species Toxicity Test Indicator was used to estimate the sensitivities of test species that were either resident or commonly used as surrogates for Lower San Francisco Bay to copper and nickel in laboratory water. The endpoints of this indicator, expressed as an acute LC<sub>50</sub> (the toxicant concentration that caused mortality in 50% of the test organisms) were used in the Aquatic Ecological Risk Assessment Protocol (AERAP) Indicator to estimate the local community response at six different levels of protection. The AERAP Indicator used regression analysis to provide a range of copper concentrations (Effects Risk Concentration – ERC) that were based on a desired level of protection. Each of the AERAP ERC's was then multiplied by the endpoint of the Site-Specific Studies. This endpoint, called a Water Effects Ratio (WER), provided a site-specific correction factor that was used to produce a range of technically sound site-specific water quality objectives for the Lower South San Francisco Bay.

#### Assessment of Certainty

The findings of the impairment assessment for both copper and nickel are not unequivocal and include some level of uncertainty. The three primary areas of uncertainty were the toxicity of copper to phytoplankton, biogeochemical processes, and sediment toxicity in Lower South San Francisco Bay. These uncertainties may be resolved with information generated from the recommended special studies. The purpose of these studies is to reduce the identified uncertainties and to provide a more complete understanding of the existing information on the toxicity of copper and nickel to sensitive phytoplankton species, the biogeochemical processes that affect ambient concentrations and bioavailability of copper and nickel, and the causes of sediment toxicity in the Lower South San Francisco Bay.

#### Recommendations

This report presents 1) the findings of the copper impairment assessment and a range of scientifically defensible site-specific water quality objectives for copper, 2) the findings of the nickel impairment assessment and a range of scientifically defensible site-specific water quality

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objectives for nickel, and 3) a recommendation for updating the 303(d) listing for the Lower South San Francisco Bay.

#### 1 Copper Impairment Assessment and Recommended Range of SSO's

The results of the impairment assessment for copper support the following finding:

Impairment to the Beneficial Uses of Lower South San Francisco Bay due to ambient copper concentrations is unlikely.

An important component of the impairment finding was the extrapolation of laboratory toxicity data to the ambient environment. Water effects ratios (WER) were an important tool in reducing the uncertainty associated with the extrapolation of laboratory toxicity values to the ambient environment. These methods allowed for modifications to the national criterion by using a site-specific multiplier, which accounts for ambient water quality characteristics that may affect the bioavailability of copper. The results of this work support the WER values developed by the City of San Jose and the corresponding site-specific water quality objective values for dissolved copper ranging from 5.0 to  $12.0 \,\mu g/L$ .

#### 2 Nickel Impairment Assessment and Recommended Range of SSO's

The results of the impairment assessment for nickel support the following finding:

Impairment to the Beneficial Uses of Lower South San Francisco Bay due to ambient nickel concentrations is unlikely

A combination of the indicator species and recalculation procedures were used to develop site-specific modifications to the national water quality criterion for nickel. This recalculation indicated that dissolved nickel concentrations ranging from 11.6 to 20.5  $\mu$ g/L in the Lower South San Francisco Bay would be protective of beneficial uses.

#### 3 Recommendations Relative to 303(d) Listing

The analyses presented in this report indicated that even if an SSO was established at the low end of the respective justifiable ranges for dissolved copper and nickel, such SSOs would be attained in the main water mass of Lower South San Francisco Bay. Based on the above assessment findings, it is recommended that the 303 (d) list should be updated to de-list copper and nickel as stressors for Lower South San Francisco Bay.

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#### 1.0 INTRODUCTION

The 1996 San Francisco Bay Impaired Water Body listing identified San Francisco Bay below the Dumbarton Bridge (Lower South San Francisco Bay) as a high priority impaired water body. Metals were noted as the pollutant of concern and municipal point sources, urban and storm runoff and surface mining were identified as the sources of pollutants. An updated listing for the Lower South San Francisco Bay was prepared in early 1998 by the staff of the San Francisco Regional Water Quality Control Board (RWQCB). The 1998 303(d) list (letter, Alexis Strauss, U.S. EPA 5-12-99), recently approved and published by the U.S. Environmental Protection Agency (EPA), specifically identifies copper, nickel, and mercury as high priority metals of concern, and selenium as a low priority metal of concern for the Lower South San Francisco Bay.

The purpose of this report is to present new information and to re-evaluate the determination that the beneficial uses of the Lower South San Francisco Bay are impaired due to ambient concentrations of copper and nickel. This report is intended to provide policy makers, regulators, and stakeholders with the most current laboratory and ambient information available to compare with known threshold impact levels on selected indicators. The goals of this beneficial-use impairment assessment are to:

- Compile and evaluate data on ambient concentrations and toxicity information for copper and nickel in the Lower South San Francisco Bay
- Identify, evaluate and select indicators of beneficial-use impairment
- Develop endpoints for the selected indicators that can be used to assess the existence of impairment and compare these values to ambient concentrations in the Lower South San Francisco Bay
- Assess the level of certainty with which it can be shown ambient concentrations of copper and nickel are or are not resulting in beneficial-use impairment
- Recommend numeric values for the TMDL Work Group to consider as site-specific objectives for dissolved copper and nickel in the Lower South San Francisco Bay

Prior to presenting the results of the impairment assessment, some important background information is reviewed. This information includes a summary of the regulatory framework that defines the listing process for impaired water bodies. In addition to the EPA guidelines, the San Francisco Bay Basin Plan and the designated beneficial uses of the Lower South San Francisco Bay are described. These elements of the regulatory framework are important in determining how the results of the impairment assessment can be used to establish a sound technical basis for setting water quality objectives for the Lower South San Francisco Bay. Other background information in this section includes a brief description of the linkage between the impairment assessment and other efforts that are underway in this project – Calculation of Total Maximum Daily Loads (TMDLs) for Copper and Nickel in Lower South San Francisco Bay. The potential

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outcomes of this impairment assessment are also described. Finally, short descriptions of the individual sections of this report are presented below.

#### 1.1 Regulatory Framework

The primary aspect of the regulatory framework and the reason that this impairment assessment is being conducted is the 303(d) list of impaired water bodies described above. However, other important elements of the regulatory framework include 303 (d) listing/delisting procedures, beneficial use definitions, and procedures for establishing site-specific objectives for the Lower South San Francisco Bay. Basic summary information on these elements is presented below. How this impairment assessment can make a contribution to the implementation of the Basin Plan is also described.

#### 303 (d) Listing Guidance

The guidelines for conducting the 1998 listing in California to meet Section 303(d) requirements of the Clean Water Act (CWA) address topics such as listing and delisting factors, scheduling and prioritization, public notice procedures and coordination with the State Board's watershed management initiative program. Of particular importance to the copper and nickel assessment of impairment are the key listing and delisting factors. Key listing factors include:

- Beneficial uses are impaired or are expected to be impaired within the listing cycle<sup>1</sup>.
- The water body is on the previous 303(d) list and either: (a) "monitored assessment" continues to demonstrate a violation of objective(s) or (b) "monitored assessment has not been performed.
- Data indicate tissue concentrations in consumable body parts of shellfish exceed applicable tissue criteria or guidelines.

Delisting factors<sup>2</sup> in the guidelines include:

- Objectives are revised and the exceedance is thereby eliminated.
- A beneficial use is de-designated after US EPA approval of a Use Attainability Analysis (UAA), and the non-support issue is thereby eliminated.
- Faulty data led to the initial listing.
- It has been documented that the objectives are being met and beneficial uses are not impaired based upon monitored assessment criteria.

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The guidelines indicate that impairment is based upon evaluation of chemical, physical, or biological integrity and that impairment will be determined by "qualitative assessment." Qualitative assessment is defined as an assessment based upon information other than ambient monitoring data such as land use data, water quality impacts, and predictive modeling. The guidance specifically states that "sole reliance on professional judgment, literature statements (often judgment based), or public comments should not be the only basis for listing."

<sup>&</sup>lt;sup>2</sup> The guidelines indicate that water bodies may be delisted for specific pollutants or stressors if any one of the factors is met.

The listing document also contains guidance on criteria to use to define priority ranking for listed waters. These criteria include: significance of the water body, degree of impairment, conformity with related activities, potential for beneficial use protection or recovery, degree of public concern, and available information. This information is important because one of the goals of this impairment assessment is to re-evaluate whether the beneficial uses of the Lower South San Francisco Bay are being impaired due to ambient copper and nickel concentrations.

#### RWQCB Basin Plan and Beneficial Uses

The Regional Board adopted its first Water Quality Control Plan for the San Francisco Bay Basin (Basin Plan) in 1975. The most recent revision to the Basin Plan was adopted on June 21, 1995. This updated and consolidated Plan represents the Board's master water quality control planning document. The revised Basin Plan was approved by the State Water Resources Control Board (State Board) and the Office of Administrative Law on July 20, 1995, and November 13, 1995, respectively.

The Basin Plan defines beneficial uses and water quality objectives for waters of the state in the San Francisco Bay Region, including surface waters and groundwaters. The beneficial uses cited in Chapter 2 of the 1995 Basin Plan applicable to the Lower South San Francisco Bay are listed below.

- Water contact recreation
- Non-contact water recreation
- Wildlife habitat
- Preservation of rare and endangered species
- Estuarine habitat
- Fish migration
- Fish spawning (potential use)
- Industrial service supply
- Shellfish harvesting
- Navigation
- Commercial and sport fishing

These beneficial uses provide the basis of the copper and nickel impairment assessment, and they are discussed in detail in Section 2 of this report. The results of the impairment assessment can be used to evaluate the existence of impairment today as well as the development of scientifically based water quality objectives (WQOs) for the Lower South San Francisco Bay that can be used to regularly evaluate the maintenance of beneficial uses.

#### Lower South San Francisco Bay Regulatory Challenge and Opportunity

The regulatory perspective and sensitivity of the ecological system in the Lower South San Francisco Bay is stated in the Regional Board's Basin Plan (p. 3-2) as follows:

"The Lower South San Francisco Bay below the Dumbarton Bridge is a unique, water-quality limited, hydrodynamic and biological environment which merits continued special attention by the Regional Board. Site-specific water quality objectives are absolutely necessary in this area

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for two reasons. First, its unique hydrodynamic environment dramatically affects the environmental fate of pollutants. Second, potentially costly nonpoint source pollution control measures must be implemented to attain any objectives for this area. The costs of these measures must be factored into economic impact considerations by the Regional Board in adopting any objectives in this area. Nowhere else in the region will nonpoint source economic considerations have such an impact on the attainability of objectives."

The regulatory challenges facing the Lower South San Francisco Bay, and a roadmap for addressing them, are described in the Revised Watershed Management Initiative (WMI) Bay Monitoring and Modeling Subgroup (BMM) Work Plan (November 5, 1998). The challenge is to establish a sound technical basis for management of the Lower South San Francisco Bay including municipal wastewater and stormwater permit requirements that are protective of beneficial uses, effective, and not prohibitively expensive. This includes:

- Assessment of the beneficial uses of the main water mass and slough areas;
- Consideration of water quality objectives;
- Development of a Total Maximum Daily Load (TMDL); and
- Development of associated Wasteload Allocation /Load Allocation (WLA/LA) for pollutants causing impairment of the Lower South San Francisco Bay.

The results of this impairment assessment provide a unique opportunity to resolve long-standing issues and to develop site-specific water quality objectives for copper and nickel in the Lower South San Francisco Bay. Recommended ranges of site-specific objectives (SSOs) for copper and nickel in the Lower South San Francisco Bay are presented in Section 5 of this report.

#### 1.2 Copper and Nickel TMDL Project

In January 1998, a 4-year project was initiated to develop copper and nickel TMDLs for the Lower South San Francisco Bay. The TMDL project is one of the most comprehensive, chemical-specific, environmental assessments ever conducted in San Francisco Bay. In addition to this impairment assessment, there are three related technical efforts underway:

- Development of a Conceptual Model for Copper and Nickel in the Lower South San Francisco Bay
- Assessment of Pollutant Levels and Sources
- Evaluation of Existing 2-D /3-D Models

As part of the TMDL project, the development of the copper and nickel TMDLs is also being integrated into the ongoing Santa Clara Basin Watershed Management Initiative (WMI), and a major emphasis is being placed on establishing and maintaining public and industry involvement. One indication of the collaborative aspect of this effort is the formation of the TMDL Work Group (TWG) to which this report is being submitted. Project Plans to guide the work effort on the above key issues have also been reviewed and approved by the TWG. This assessment effort is described in the TMDL Project Plan for Task 2.

Conducting the TMDL is a State requirement, and there is optimism that these TMDLs will provide a unique opportunity to address the many complex issues associated with setting water

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quality objectives for the Lower South San Francisco Bay. Several stakeholders have noted that the collaborative approach that is being taken to prepare the TMDLs is likely to be more successful than the programmatic approach that has traditionally been used by state and local regulatory agencies.

#### 1.3 General Impairment Assessment Approach

This beneficial use impairment assessment report is intended to provide the TMDL Work Group with the best technical laboratory and ambient information currently available to compare with known threshold impact levels on selected indicators. Potential categories of parameters and criteria include toxicity (acute/chronic), biological (biota composition, health, abundance, and physical habitat vs a reference site), chemical (numeric values), and physical (capacity to support uses).

A companion report to this assessment, "Sources and Loadings of Copper and Nickel to South San Francisco Bay (URS Griener Woodward Clyde, Tetra Tech, 1999)" summarizes available information on copper and nickel sources, loading, and ambient water column and sediment concentrations. A second companion report, "Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay (Tetra Tech, 1999)", qualitatively depicts the current understanding of cycling processes and associated uncertainties. This conceptual model is necessary to help understand the multitude of interrelated pathways and mechanisms that can potentially affect impacts on beneficial uses. It also provides a framework for translating effects on individual indicator organisms to effects (impacts) on the health and integrity of the overall Lower South San Francisco Bay ecosystem.

This Impairment Assessment uses a "weight of evidence" technical approach that differs from the U.S. EPA's definition of the term. The term as used in this Assessment Report means that all available evidence is reviewed and incorporated in proportion to its applicability, technical certainty, statistical robustness, etc. in evaluating likely impacts and impairment of beneficial uses. In general, "suites" of indicators are believed to more accurately characterize ecosystem health and impairment than single indicators/organisms. This approach is consistent with EPA's 305(b) guidance regarding "integrated assessment."

This report is intended to help reviewers become familiar with the existing data and evaluate the impairment assessment approach for the Lower South San Francisco Bay. This report provides best professional estimates of the 1) relative significance of individual parameters in the assessment analysis, and 2) the relative uncertainty associated with each assessment parameter. Also provided are recommendations for additional data collection, analysis, and stakeholder based policy development. The results of the impairment assessment can be used to evaluate the existence of impairment today as well as the development of scientifically based WQOs for the Lower South San Francisco Bay that can be used to regularly evaluate the maintenance of beneficial uses.

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#### 1.4 Assessment Potential Outcomes

This assessment was designed to provide information necessary to help evaluate whether or not beneficial uses are currently being impaired in the Lower South San Francisco Bay. This assessment describes and updates the data used for prior 303(d) listings and adds statistical summaries and information on the relative importance and uncertainty associated with the various data.

The following potential conclusions and outcomes to the beneficial use impairment assessment were considered as part of developing the impairment assessment findings.

- No impairment: A finding of no impairment requires a high level of certainty regarding assessment results. The lines of evidence and indicators would unequivocally demonstrate no negative impact to beneficial uses due to copper and nickel. In addition, the lines of evidence and indicators would affirm ecosystem integrity and a quantitative assessment of the status of beneficial uses under current and projected (within the current permitting cycle) loading of copper and nickel. This finding would be based on a large quantity of documented data for multiple lines of evidence and or indicators, each providing consistent results.
- Impairment unlikely: This finding requires clear support from more than one line of evidence and is based on a substantial amount of laboratory and or environmental data. This level of finding does include uncertainties regarding the finding. It is necessary to describe and define the consequences of identified uncertainties. It is also suggested that the uncertainties be addressed through recommended studies.
- **Possible impairment:** A possible impairment finding requires that a line of evidence or indicator suggests diminished ecosystem integrity that causes a negative impact on any designated beneficial use from copper or nickel. Possible impairment can be due to existing loadings or expected future loadings of copper or nickel. There are uncertainties associated with this finding that must be described with additional studies designed to confirm the existence and/or level of impairment.
- **Definite impairment:** The lines and evidence and indicators clearly indicate negative impact on designated beneficial uses due specifically to ambient concentrations of copper and nickel. There is substantial documented data to support the finding and there are few if any uncertainties associated with the assessment conclusion.
- Cannot determine impairment: This finding does not indicate impairment or nonimpairment of the designated beneficial uses. The uncertainties are due to inadequate data, lack of knowledge regarding basic processes or status of resident aquatic life and wildlife populations. This finding requires a significant commitment of resources for monitoring and special studies to better determine the status of beneficial uses and the extent and magnitude of stressors (i.e., copper and nickel).

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#### 1.5 Assessment Report Organization

Section 1 provides background on the assessment, including the regulatory basis for and constraints of this assessment, and the context within which potential outcomes will be evaluated. Section 2 provides an overview of the beneficial-use assessment strategy. Emphasis is placed on describing the role of indicators in the assessment strategy and steps that have been taken to identify and evaluate the use of indicators to identify the existence of or potential for beneficial-use impairment. Section 3 describes ambient conditions in the Lower South San Francisco Bay. Water quality, sediment, and toxicity data are compiled and evaluated. Section 4 describes a set of four indicators that were selected for detailed evaluation. A synthesis of the impairment assessment, the description of potential site-specific objectives, and recommendations for special studies are provided in Section 5. The recommendations in Section 5 are based in part on assumptions and determinations that required judgment by the technical consultants. Section 6 discusses the key risk management (i.e., policy) decisions the TWG needs to make in light of these recommendations.

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### 2.0 ASSESSMENT STRATEGY: BENEFICIAL USES AND INDICATORS

The goals of the beneficial-use impairment assessment are focused around the development and application of a set of environmental indicators. The development process begins with the compilation and critical evaluation of information on the performance of environmental indicators that have been used or are suitable for use in Lower South San Francisco Bay. The next step is the application of these indicators to assess the existence of impairment, where the assessment is based on determining if the designated beneficial uses have been impaired in Lower South San Francisco Bay by ambient copper and nickel concentrations. The ultimate goal is to develop numeric values for the selected indicators that can be used as site-specific water quality objectives for copper and nickel.

#### 2.1 Indicators and Their Role

The status of the Beneficial Uses of Lower South San Francisco Bay (described below) is difficult to measure directly, and there is a recognized need for a set of environmental indicators that can be used to assess the existence and maintenance of these beneficial uses. These environmental indicators are defined as measurable quantities that are so strongly associated with particular environmental conditions that the value of the measured quantity can be used to indicate the existence and maintenance of these conditions. This definition has three main elements: the measurable quantity, the value of the quantity, and the environmental condition.

The measurable quantity can be an organism, an ecological community, or measures of biogeochemical conditions. The following quantities have been used previously as indicators for ecological assessment:

- Response of an individual species to a particular pollutant
- Presence or absence of sensitive species
- Index of community taxa (e.g., diversity indices)
- Rate of a process (e.g., nutrient uptake);
- Level of a pollutant in solution, sediment, and tissue phases
- Birth or mortality rate of resident populations
- Age structure of a population

Each of these and other indicators has been shown to exhibit specific responses to either existing conditions or environmental interventions (e.g., increasing or decreasing pollutant loads).

The value of the measurable quantity is an important part of this definition. It denotes that there can be a quantitative relationship between the indicator and the environmental condition. It is not strictly the presence or absence of an organism, for example, that indicates the existence of the environmental condition. In this assessment there is an emphasis placed on defining values of candidate indicators. The ultimate goal is to develop numeric endpoints for the selected

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indicators that can be considered as site-specific objectives for copper and nickel in Lower South San Francisco Bay.

The fact that the environmental conditions referred to in the definition of environmental indicators can be defined makes this impairment assessment feasible. These conditions are the designated beneficial uses that are defined in the Basin Plan. The Beneficial Uses believed to be most sensitive to potential impacts from ambient concentrations of copper and nickel because of their substantial aquatic life components are: Shellfish Harvesting, Commercial and Sport Fishing, Fish Migration, Fish Spawning, Wildlife Habitats, Preservation of Rare and Endangered Species, and Estuarine Habitat. The challenge is to define the indicator or set of indicators that are strongly associated with these beneficial uses.

The assessment approach is illustrated in Figure 2-1 using Estuarine Habitat as the example assessment endpoint. The second column of the figure identifies example environmental indicators that could be used to characterize existing conditions for Estuarine Habitat. The environmental indicators to be selected will measure key aspects of the Beneficial Use (e.g., population and distribution of desired species). The effectiveness of an indicator is increased when it can be used to interpret the magnitude and significance of the effect of a specific stressor (e.g., elevated concentrations of copper and nickel) on a Beneficial Use. Available information is used to determine the impacts to Beneficial Uses that can be attributed to copper and nickel. The third column of the figure summarizes the data or information requirements of each environmental indicator. The fourth column represents the final phase of the proposed strategy to evaluate or recommend numeric endpoints/targets for the TMDL that could also be used as site specific objectives for the TMDL for the Lower South Bay.

#### 2.2 Impairment Assessment Strategy

There are four primary aspects to the impairment assessment strategy that are presented in this report:

- 1. Identification and evaluation of indicators
- 2. Compilation and evaluation of information on ambient conditions in Lower South San Francisco Bay
- 3. Quantification of uncertainty in all measured values
- 4. Development of a range of values that could serve as site-specific water quality objectives for copper and nickel

The identification and initial evaluation of indicators is described in Section 2.3. Initially, a workshop was held in January 1999 to describe candidate indicators and the use of these indicators in the impairment assessment process. Based on information presented at this workshop, a primary set of indicators was defined. In Section 4 of this report each of primary indicators is evaluated in more detail.

A substantial effort has been made to obtain data on ambient conditions in the Lower South San Francisco Bay. Each of the primary indicators is evaluated in more detail in Section 4 of this report.

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The consequences of the decisions that are made regarding the setting of site-specific objectives extend well into the future. For this reason, it is essential that predictions of the effects of allowable concentrations of copper and nickel in Lower South San Francisco Bay are accurate. However, the presence of uncertainty complicates the ability to make accurate predictions of environmental effects. Furthermore, without a measure of the magnitude of the uncertainty associated with decision criteria, decision-makers are unable to effectively weigh and use the results of environmental analyses. These issues are addressed in the impairment assessment by making a vigorous effort to identify the magnitude and sources of uncertainty associated with each of the indicators that are used in the impairment assessment and that are used in the development of alternatives for site-specific objectives.

Uncertainty is defined herein as the state or condition of incomplete or unreliable knowledge. For each indicator evaluated or analysis conducted in this assessment, both the sources and the magnitude of known uncertainties are identified. The sources include natural variability, sample variability, and the appropriateness of models that are used in making predictions. Ideally, the magnitudes of identified uncertainties are addressed using descriptive statistics and by setting confidence limits on predicted values. In the absence of quantitative information, a professional judgement of the value of the existing information is presented.

The ultimate product of the impairment assessment is a set of recommended criteria that can be used to evaluate evidence of impairment to determine whether the Lower South San Francisco Bay should remain on the 303d (d) list for copper and nickel and propose SSOs for copper and nickel that are protective of the sensitive beneficial uses in the Lower South San Francisco Bay.

#### 2.3 Proposed Indicators

The impairment assessment was conducted using the following guidelines to ensure that the results provide the TWG with a consistent and objective product.

- 1. All indicators will be evaluated using the same criteria.
- 2. The methods and data used by an indicator must be documented.
- 3. Indicators should be used in combination with other indicators. Assessment results and recommendations should be based on more than one indicator.
- 4. The full range of estimated effects for each indicator should be presented.
- 5. Uncertainties, to the extent possible, should be identified and remedies described.

Seven indicators were considered for inclusion in the impairment assessment. The proposed indicators include: Individual Species Toxicity Tests, Aquatic Ecological Risk Assessment Protocol, Site-Specific Studies, Plankton, Simultaneously Extracted Metals/Acid Volatile Sulfides, Benthic Macroinvertebrates, and Charismatic Macrofauna— Harbor Seals. Based upon stakeholder recommendations the Palo Alto Clam Study was added to Benthic Macro Invertebrates, and Birds were added to Charismatic Macrofauna. Each indicator was evaluated using the criteria listed in Table 2-1. The results of these evaluations are included in Appendix A. A brief summary of each indicator is included below. It is important to note that even if an indicator was not formally included in the impairment assessment, knowledge about the

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#### Table 2-1 Indicator Evaluation Criteria for South San Francisco Bay Impairment Assessment

- 1. How clearly is the proposed indicator linked to one or more of the sensitive Beneficial Uses?
- 2. How strongly linked is the indicator to potential effects of copper and nickel?
- 3. What other stressors does the indicator respond to?
- 4. Does the proposed indicator provide an accurate representation of environmental conditions?
- 5. Does the indicator communicate with Initiative TMDL stakeholders?
- 6. Does the indicator have broad scientific acceptance?
- 7. Is the indicator measurable in the South Bay?
- 8. Is the indicator easy to use and inexpensive?
- 9. Is there adequate information available to support the use of the indicator?
- 10. Can the indicator be used in combination with other indicators?
- 11. What are the uncertainties associated with the use of this indicator?

candidate indicator was still used as information in the assessment and any subsequent SSO recommendations. Thus, the information was not explicitly excluded from the assessment, but was not sufficient to be used as an indicator.

**Individual Species Toxicity Tests:** This indicator utilized the toxicological responses of the individual organisms listed in the National Water Quality data set to either copper or nickel. Their responses provided a measurable quantity (sensitivity endpoint), the value of which could be used to assess the potential for impairment of Beneficial Uses under specific water quality conditions (e.g., laboratory water). Individual species are a component of the aquatic life, which is essential to each Beneficial Use. Understanding the range of responses of individual species to dissolved copper can be used as an indicator for evaluating the impact of ambient concentrations on Beneficial Uses and can be used to characterize the preferred range for dissolved copper and nickel (i.e., recommended SSOs).

Laboratory toxicity testing data was compiled from literature sources for a wide range of species that are either indigenous to San Francisco Bay or a close surrogate (i.e., east coast genus of genus occurring in South San Francisco Bay). Toxicity data was obtained on organisms representing most ecological niches in the South Bay. Information was compiled on 46 species for copper (137 total tests) and 27 species for nickel (49 total tests). The information has been compiled in a table to facilitate review.

To be considered unimpaired a Beneficial Use requires the survival of organisms normally associated with estuarine habitats. Some of the species listed on the table should be considered as a primary indicator or attribute of a Beneficial Use. In the case of salmonids, the measure of the toxicity of the water column copper concentrations will determine whether the migration of fish into the estuary from tributaries and out of the estuary into the tributaries has been blocked by a "toxicity barrier". Specific emphasis will be placed on potential barriers to juvenile salmonids migrating from the freshwater tributaries into the estuary since salmonids are more

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sensitive to toxicants while juveniles than as adults. Species tolerances can also help determine if an important estuarine habitat function has been impaired due to toxicity. The Individual Species Toxicity Tests is recommended as an assessment indicator and is described in greater detail in Section 4.1.

Aquatic Ecological Risk Assessment Protocol (AERAP): This indicator utilized the toxicological responses of the individual organisms listed in the National Water Quality data set to copper, much like the Individual Species Toxicity Tests Indicator. The AERAP Indicator, however, was not used to assess the responses of organisms to nickel because its use would not add to either the results reported in the City of San Jose's recalculation study, or our current understanding of nickel toxicity to aquatic organisms. In contrast to the Individual Species Toxicity Tests Indicator, the AERAP indicator was used to assess the data set on a community basis. In this case, the responses provided a measurable quantity (ERC), the value of which could be used to assess the potential for impairment of Beneficial Uses under specific water quality conditions (e.g., laboratory water). This indicator provides a measure of the assemblage of species necessary to support a dynamic and productive trophic structure. This indicator builds on the individual species toxicity tests by evaluating the ecologically relevant measure of community status.

The Aquatic Ecological Risk Assessment Protocol is a synthesis analysis of individual species toxicity tests to create a community level risk estimate of effects from water column and sediment pollutants. The protocol combines information from a toxicity database (for copper) with environmental concentrations of these pollutants. The protocol applies a logistic regression model to the toxicity and exposure data distributions to generate cumulative frequency curves of the probability of predicted impact to the modeled community. Toxicity data for resident species were incorporated into the model. The model can be used to test risk evaluations at specified level of protection (i.e., protective of 95% of community taxa), and evaluate risk posed by ambient concentrations of copper through its hypotheses testing function. This indicator provides a useful interpretation of the single species toxicity data used in the laboratory toxicity indicator. The AERAP is recommended as an assessment indicator and is described in greater detail in Section 4.2.

Site-Specific Studies: This indicator utilized the toxicological responses of the most sensitive organisms listed in the National Water Quality data set to either copper or nickel in ambient Lower South San Francisco Bay water. Their responses provided a measurable quantity (sensitivity endpoint), the value of which could be used to assess the potential for impairment to Beneficial Uses under site-specific water quality conditions. Site-Specific Studies are a measure of environmental conditions (i.e., local biological and water quality characteristics) that can either mitigate or enhance the toxicity of dissolved copper and nickel. The three forms for deriving the indicator value include: 1) Recalculation Procedure, 2) Indicator Species Procedure, and 3) Resident Species Procedure. Three site-specific studies have been completed in South San Francisco Bay providing the assessment with substantial quantities of information to develop this indicator. The purpose of the site specific studies was to determine whether national water quality criteria for copper and nickel are appropriate for Lower South San Francisco Bay. The site-specific studies take the laboratory studies one step closer to the environment by using ambient South Bay water instead of laboratory water. Using ambient water provides an estimate of the complexing capacity (and, therefore the amount of copper or nickel that is bioavailable)

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that is present on a site-specific basis. This provides a more realistic assessment of potential impairment due to ambient concentrations of copper and nickel. This indicator is recommended for use in the impairment and is described in more detail in Section 4.3.

**Plankton:** Plankton as an indicator provides qualitative information regarding the role of dissolved copper and nickel in some of the basic ecological processes occurring in Lower South San Francisco Bay. These processes include primary productivity, biogeochemical cycling (copper uptake), and apparent complexing capacity. In addition, this indicator provides some additional information on the potential sensitivity of primary producers to copper and nickel. Plankton have been selected as a candidate indicator because of their importance as the base of the food chain that supports all of the beneficial uses being considered in the assessment. The general information on plankton ecology helps to inform the use of other indicators. However, plankton populations are difficult to monitor and San Francisco Bay does not have a comprehensive plankton monitoring program that can support a full characterization of baseline or trends in plankton assemblage status. Factors that are considered in the assessment include:

- Evaluation of calculated free ion copper concentrations in the Lower South San Francisco Bay and its potential effects on cyanobacteria, coccolithophore, dinoflagellate, and diatom growth rates;
- The effect of an EDTA like compound, which is a chelator of metals, that is present
  in Lower South San Francisco Bay as a result of its use and discharge from the
  microelectronics industry;
- The capability of phytoplankton to exude small amounts of an organic chelator for copper;
- Evaluation of the relative amounts of copper and binding ligands in South San Francisco Bay;
- Evaluation of calculated free ion concentrations for copper in San Francisco Bay and its potential effect on cyanobacteria and coccolithophores; dinoflagellate growth rates; and diatoms;
- Evaluation of the effects curve for diatoms and other phytoplankton species;
- Consideration of the relationship between competitive ions (e.g., manganese, zinc, silica, and iron) and copper toxicity due to competition for cellular receptor sites.

Evaluation of population abundance and assemblages would require an extensive monitoring program. Diatoms are the essential component of the phytoplankton assemblage for supporting the food chain. This is a key indicator because of its position as the base of the food chain. However, there is an inadequate amount of monitoring information to fully develop a phytoplankton community / population indicator. It is important to note that the information on plankton can be used to help interpret other indicators but plankton is not recommended as a primary indicator in this assessment. The reasoning behind this decision is described in greater detail in Section 4.4.

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#### Benthic Macroinvertebrates

The benthic macroinvertebrate indicator is based on information from the RMP Benthic Pilot Study. Benthic macroinvertebrates can provide excellent insights into the environmental health of an ecosystem. There are several assessment methods in use around the country that rely on various measures of the benthic macroinvertebrate community. The best known assessment is based on evaluation of "assemblages" of species within a particular habitat type. There are three assemblages for South Bay 1) Fresh Brackish, 2) Estuarine, and 3) Central Bay. Reference sites are being developed for these assemblages. To use benthic macroinvertebrates as an effective indicator requires knowledge of reference conditions within an unimpacted area. The reference sites are used to compare with assessment sites to evaluate differences. The comparison of assessment areas with reference sites is based on the frequency of occurrence of "pollutant-sensitive" species versus "pollutant-tolerant" species. The reference assemblages for Lower South San Francisco Bay are not completed and are not available for use in this assessment. It is unclear how benthic macroinvertebrates can be used in the impairment assessment.

Benthic macroinvertebrates are a useful indicator for overall ecosystem health, but are difficult for assessment of a single stressor. Many of the stressors and pollutants in the bay covary – meaning that it would be difficult to attribute or identify an impact to a single cause. This indicator won't work for just copper and nickel. The best use of this indicator would be to confirm impacts that were predicted by indicators that had a tighter linkage to copper and nickel. An evaluation of the Palo Alto Clam (*Macoma balthica*) studies (Hornberger, et al 1998; Luoma, et al 1998b) has been included as Appendix B. These studies reported that sediment and bivalve (*Macoma balthica*) tissue concentrations of copper and silver decreased as point source discharges of these metals from the Palo Alto Water Quality Control Plant (PAWQCP) declined. As a result, clam populations on the Palo Alto mudflats made a "come-back". Loads of copper from the PAWQCP have continued to decline steadily between 1991 and 1997, however, copper concentrations in the bivalve tissues have increased slightly during this time period. This indicates that some unknown local processes are affecting metal uptake and making it more difficult to determine a direct linkage between copper concentrations in the water and sediments and concurrent bivalve tissue copper concentrations.

The measures of benthic macroinvertebrate community are considered to be a valuable supporting indicator. That is, are the toxic effects predicted by toxicity tests actually observed? However, a characterization of a reference condition assemblage for Lower South San Francisco Bay has not been completed in time to be used in this assessment. Benthic macroinvertebrates will be used in future assessments, but are not recommended nor used for this assessment.

Ratio of simultaneously extracted metals to acid volatile sulfides (SEM/AVS)

SEM/AVS was used by U.S. EPA to develop sediment quality criteria. The SEM/AVS ratio is based on the same concepts used by sediment equilibrium models to estimate the bioavailability of non-ionic organic compounds in sediments. Acid-volatile sulfide binds divalent cationic metals on an equimolar basis producing metallo-sulfides, which are generally accepted as being non-bioavailable and therefore less toxic. Sediment samples are taken and transferred to the

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laboratory for the chemical analysis procedure. The procedure was developed and has been used on the east coast. Several laboratory toxicity studies have verified the ability of the method to predict both toxicity and non-toxicity of sediments. However, there is a continuing debate regarding whether the method predicts potential bioavailability versus actual bioavailability. The distinction is that sediment dwelling organisms disturb the sediment environment (introducing oxygen) which creates different conditions than the method assumes exists. Also some biologists suggest that the internal environment of organisms that have ingested sediments do not match the environmental conditions upon which the test is based. Those not supporting SEM/AVS state that the laboratory toxicity tests do not accurately simulate conditions in the environment (e.g., unconsolidated sediment versus intact sediment). However, several validation studies demonstrated a high correlation between both predicted toxicity and predicted nontoxicity with the paired laboratory toxicity tests. The method has been used to assess the effects of the sediment SEM/AVS ratio to the ability of benthic organisms to bioaccumulate four metals (cadmium, silver, nickel, and zinc) present in San Francisco Bay sediments (Lee, et al. 1999, inpress). This study reported that, while metal concentrations in sediment porewater may be controlled by sediment sulfide-metal equilibria, metals exposure is not controlled simply by porewater concentrations, but by particle ingestion as well. These uncertainties associated with the SEM/AVS procedure make it a poor choice as an indicator of potential metals toxicity to benthic organisms. This, as well as other uncertainties (e.g., limited knowledge of the effects of benthic invertebrates on copper and nickel remineralization from suspended particles during filtration and digestion, benthic bioturbation/irrigation effects on sediment release fluxes (biologically enhanced advection), and the lack of knowledge on adsorption/desorption kinetics and the release of metals from resuspended sediments) preclude the use of SEM/AVS as an indicator of impairment for this assessment.

Charismatic Macrofauna: Harbor Seals and Birds: This indicator was evaluated to provide consideration of larger vertebrates and higher order predators

**Harbor Seals** – Lower South San Francisco Bay provides habitat for the primary breeding colony of harbor seals (*Phoca vitulina richardii*) in San Francisco Bay. Recent counts of harbor seal populations in San Francisco Bay indicate a downward trend when compared to previous studies. This is in contrast to harbor seal population increases found in other parts of the State (e.g., Point Reyes). Studies of harbor seal population trends in other parts of the world have indicated that seal deaths and reduction in the number of viable pups co-occur with the presence of organic toxicants and heavy metals in seal tissues. It should be noted, however, that no direct linkage has been identified by the technical team between copper and nickel tissue concentrations and deleterious effects to harbor seals.

The following review was submitted by Dianne Kopec, Director San Francisco Bay Harbor Seal Project:

The resident harbor seals of San Francisco Bay have been recommended as an environmental indicator in establishing regional TMDL limits for toxic contaminants in the South Bay. In general this is a excellent suggestion since past studies already document that certain contaminants accumulate to toxic levels in San Francisco Bay harbor seals, suggesting that the seals and other higher trophic level organisms would benefit from a more regional specific control on discharge of these contaminants. However, as mammals, the sensitivity of harbor

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seals to potentially toxic contaminants varies, making them a poor indicator species for certain contaminants.

Research on the population dynamics of the resident harbor seals in San Francisco Bay indicate that the majority of harbor seals live year-round within the waters and shorelines of San Francisco Bay. Radiotelemetry studies documented limited exchange between SF Bay harbor seals and those living along the central coast of California. Within the Bay, strong site fidelity was found during the spring and summer months with an increase in seal movements between different parts of the Bay during the fall and winter. Radio-tracking also identified specific harbor seal foraging areas at sites within the central and southern portions of San Francisco Bay. Scat analyses revealed the dominant harbor seal prey species consumed seasonally within the Bay. These findings support the position that, overall, harbor seals are useful indicators of environmental quality within San Francisco Bay.

More specifically, harbor seals have been proposed as environmental indicators for both copper and nickel TMDLs, which are currently being developed for South San Francisco Bay. Copper is an essential element in mammals and normal copper metabolism prevents the accumulation of excess copper in mammals. Acute toxicity can occur in rare instances with ingestion of copper salts. Given that harbor seals would be exposed to copper residues through prey ingestion, there is little chance that excess copper would accumulate within individuals or that copper toxicity in harbor seals would result from chronic copper exposure. The results of copper residue analyses in harbor seal blood from SF Bay seals supports this, as the reported blood residue levels were below copper residue levels associated with acute toxicity in humans. As a result, harbor seals are not appropriate environmental indicators of impairment of the South Bay due to anthropogenic copper.

Nickel toxicity in mammals is found primarily through inhalation exposure. Ingestion of significant quantities of nickel salts can result in reproductive or developmental toxicity. However, 90% of ingested nickel is unabsorbed and excreted, and there is no evidence in humans that ingested nickel accumulates with age. Nickel has a relatively short half-life of 11 to less than 48 hours in mammalian blood. Given that ingestion is the primary route of nickel exposure for harbor seals, these mammals may not be good indicators of nickel impairment in the South Bay food web.

However, the results of harbor seal blood analyses for nickel residues is currently inconclusive. Nickel residues were quantified in 15% of the harbor seals sampled in SF Bay in the early 1990s and the quantified levels were markedly greater than blood nickel levels reported in exposed human workers. The relatively conservative quantification limit used in these reported analyses may have masked biologically meaningful residues present at lower blood concentrations. Further research is needed to determine whether nickel is present at toxic levels in San Francisco Bay harbor seals.

It should be noted that other toxic contaminants, especially lead, mercury, selenium, and organochlorines have been found at levels associated with mammalian toxicity in San Francisco Bay harbor seals. It would be extremely useful to develop TMDLs for these contaminants which would reflect regional accumulation levels in the biota and related toxicity in the resident species.

#### **Birds**

Birds are very visible inhabitants and users of Lower South San Francisco Bay and occupy every microhabitat. These microhabitats include saltwater, brackish, and freshwater marshes, mudflats, sloughs, open water, dikes and levees and provide shelter, rookeries, and feeding habitat for Lower South San Francisco Bay bird populations. Since many of these birds rely on fish and macroinvertebrates for food, the ambient water quality of Lower South San Francisco Bay may influence both food sources and bird populations.

Bird populations in Lower South San Francisco Bay and the Pacific Flyway fluctuate in response to several factors. These factors include contaminant stress, habitat loss, hunting and predation, and disease. Most species that occupy the Lower South San Francisco Bay have not been adequately studied and, therefore, long-term or recent population trends or the factors that affect population trends remain unknown. However, the available information indicates that bird population declines are most attributable to the following factors (Larry Walker Associates, et al., 1991a, b):

## Migratory birds,

- Habitat loss (drought and habitat conversion);
- Hunting;
- Disease; and
- Other factors not relating directly to the Lower South San Francisco Bay.

## Resident birds,

- Habitat loss;
- Predation by red fox (Vulpes vulpes); and;
- Contaminant accumulation

While contaminants (i.e., PCBs, mercury, and selenium) have been determined to be accumulating in bird tissues and eggs, the significance of this remains unknown (J.E. Takekawa, personal communication in Ohlendorf 1991). The main factors affecting bird populations in the Lower South San Francisco Bay are 1) habitat loss and 2) predation (Larry Walker Associates, et al., 1991a, b).

At this time, birds are not considered appropriate indicators of impairment caused by copper and nickel to Lower South San Francisco Bay because:

- There are no available data that describes the dose-response relationship for copper or nickel and bird populations observed in the Lower South San Francisco Bay.
- Based on available toxicity data for other avian species, relatively high concentrations
  of copper and nickel in drinking water or in ingested material are likely to be required

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before bird populations of Lower South San Francisco Bay are adversely affected (Table 2-2); and

• There are uncertainties associated with extrapolating the results obtained from laboratory studies to birds observed in the Lower South San Francisco Bay.

Avian toxicity data that are appropriate for use in the impairment assessment are summarized in Table 2-2. Appendix C, *Toxicity Profiles for Copper and Nickel*, provides more detailed discussions of available avian toxicity data for copper and nickel.

# Table 2-2 Summary Of NOAEL Values That Are Appropriate For Use In The Impairment Assessment For Birds.

The toxicity benchmark for copper was based on a growth study on one-day-old chicks (Mehring et al. 1960). A chronic No Observable Adverse Effects Level (NOAEL) of 33 mg[Cu]/kg-day is recommended to assess impacts to avian wildlife populations because:

- The study considered exposure over 10 weeks, during a critical and sensitive life-stage (1-day-old chicks);
- A serial dosing regime was administered and both a NOAEL and LOAEL were reported, permitting a limited characterization of a dose-relationship;
- No adverse effect on growth or survivorship was observed in 1-day-old chicks administered this dose—growth and survivorship can be used to evaluate persistence of populations; and
- An independent review by the U.S. DOE (Sample et al. 1996) supports the use of this study to assess potential impacts to avian wildlife species.

The toxicity benchmark for nickel was based on a growth and survivorship study on mallards (Cain and Pafford 1981). A chronic NOAEL of 77 mg[Ni]/kg-day is recommended to assess impacts to avian wildlife populations because:

- The study considered exposure over 90 days during a critical and sensitive developmental period (i.e., from hatching to 90 days of age);
- A serial dosing regime was administered and both a NOAEL and LOAEL were reported, permitting a limited characterization of a dose-relationship;
- No adverse effect on growth or survivorship was observed in 1-day-old chicks administered this dose—growth and survivorship can be used to evaluate persistence of populations; and
- An independent review by the U.S. Navy (1997) and U.S. DOE (Sample et al. 1996) support the use of this study to assess potential impacts to avian wildlife species.



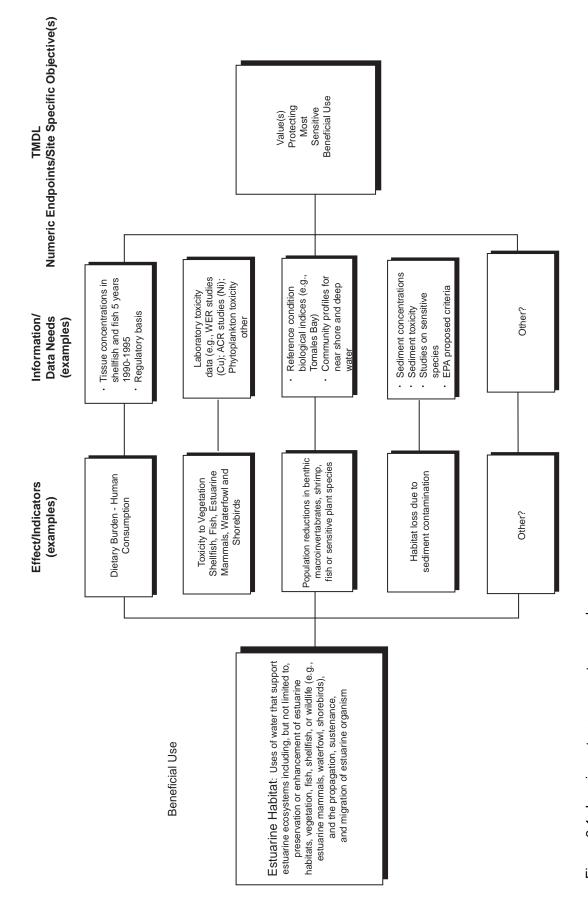


Figure 2-1. Impairment assessment approach.



# 3.0 EXISTING LOWER SOUTH SAN FRANCISCO BAY DATA: AMBIENT CONDITIONS

A substantial amount of environmental data has been collected in the Lower South San Francisco Bay over the past 10 to 20 years. These data have been collected by the POTWs as part of mandated permit studies, by the Regional Monitoring Program as part of the bay-wide effort to monitor the state of the estuary (SFEI, 1998), and as part of special studies that have been conducted to answer more focused questions. Although not all of these data have been collected to specifically address the issue of beneficial-use impairment due to copper and nickel, they do provide an excellent basis for evaluating ambient conditions and evaluating the impairment issue.

As part of this impairment assessment, a database and geographic information system have been developed in conjunction with the impairment assessment (Tetra Tech, 1998) to facilitate retrieval, display, analysis, and interpretation of these data. Specific categories of data in the database include:

- Water Quality Monitoring Data. These data consist of ambient copper and nickel concentrations in the water column measured at over 20 distinct locations in the Lower South San Francisco Bay from just north of the Dumbarton Bridge to the slough areas in the south. Over 1,700 measurements of both total and dissolved copper and nickel have been compiled. These measurements were made between 1989 and 1999.
- Sediment Quality Monitoring Data. Ambient copper and nickel concentrations in bedded sediments have been compiled from data collection efforts conducted by the RMP, the Bay Protection and Toxic Clean-up Program, and Moss Landing Marine Laboratory. These data were collected between 1994 and 1997. Data for sediment quality constituents such as oxidation-reduction potential, grain size distribution and hydrogen sulfide concentrations are also included in the database.
- **Tissue Measurements**. These data include bivalve tissue data that have been collected as part of the RMP from 1994-1997; South San Francisco Bay 1991 E5E Studies; and the results of long-term monitoring of copper concentrations in clam tissue near the Palo Alto Regional Water Quality Control Plant between 1977 and 1997.
- Water Column and Sediment Toxicity Data. Four sets of data have been compiled and evaluated. These data include the results of toxicity test that were previously performed as a basis for recommending site-specific water quality objectives for copper and nickel as well as the recent information collected by the Bay Protection and Toxic Cleanup Program and RMP's three tiered approach to assess Estuary health.

# 3.1 Water Quality Data

Four separate sets of surface water measurements of total and dissolved copper and nickel concentrations in the Lower South San Francisco Bay were considered in the assessment of ambient conditions:

	Program	Sampling Period	Total # Observations
1.	South Bay Discharge Authority (SBDA)	1989-1992	824 <sup>1</sup>
2.	Regional Monitoring Program (RMP)	1993-1997	264 <sup>2</sup>
3.	City of San Jose (WER)	1996-1997	300 <sup>3</sup>
4.	City of San Jose, South Bay (SJSB)	1997-1998	1716 <sup>4</sup>

<sup>&</sup>lt;sup>1</sup> Copper (412): 206 dissolved and 206 total. Nickel (412): 206 dissolved and 206 total.

Summary statistics for all three data sets are presented in Tables 3-1 through 3-4. The analysis of these data was separated into two phases. The initial analysis considered the SBDA and the RMP data sets. These data were collected at fixed stations three times each year, and the analysis of these data has been previously reported (SBDA, 199x and SFEI, 1997). A more detailed analysis was made of the recent SJSB data set. These data were collected bi-weekly at twelve stations in the South Bay; triplicate samples were collected at each sampling location and sampling event.

Figures 3-1 through 3-4 show the location of these sampling locations as well as the average concentrations of total and dissolved copper and nickel measured at each station. The average copper concentrations are shown in Figures 3-1 and 3-2 for the two sets of analyses. Average total and dissolved concentrations measured in the main Lower South San Francisco Bay water mass in the SBDA and RMP studies are 7.3  $\mu$ g/L (range: 3.0 to 25.6  $\mu$ g/L) and 3.6  $\mu$ g/L (range: 1.4 to 8.9  $\mu$ g/L). The average total and dissolved copper concentrations measured in the SJSB study at eight stations within the main water mass of the Lower South San Francisco Bay are 10.1  $\mu$ g/L (range: 2.3 to 107.3  $\mu$ g/L) and 2.8  $\mu$ g/L (range: 1.3 to 4.6  $\mu$ g/L), respectively. Copper concentrations measured by the RMP at stations outside Lower South San Francisco Bay are lower. To the north of the Dumbarton Bridge, concentrations are 3.4  $\mu$ g/L total and 2.4  $\mu$ g/L dissolved. Average concentrations outside the Golden Gate Bridge are 0.6  $\mu$ g/L total and 0.5  $\mu$ g/L dissolved (Conceptual Model Report, 1999).

The average nickel concentrations are shown in Figures 3-3 and 3-4. The average total and dissolved nickel concentrations measured in the main water mass of the Lower South San Francisco Bay during the SBDA and RMP monitoring programs are 12.2  $\mu$ g/L (range: 4.0 to 48.0  $\mu$ g/L) and 4.7  $\mu$ g/L (range: 1.6 to 11.8  $\mu$ g/L), respectively. The average total and dissolved nickel concentrations measured in the SJSB study at eight stations within the main water mass of the Lower South San Francisco Bay are 19.1  $\mu$ g/L (range: 2.4 to 211  $\mu$ g/L) and 3.6  $\mu$ g/L (range: 1.6 to 10.1  $\mu$ g/L), respectively.

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<sup>&</sup>lt;sup>2</sup> Copper (132): 66 dissolved and 66 total. Nickel (132): 66 dissolved and 66 total.

<sup>&</sup>lt;sup>3</sup> Copper (150): 75 dissolved and 75 total. Nickel (150): 75 dissolved and 75 total.

<sup>&</sup>lt;sup>4</sup> Copper (886): 449 dissolved and 437 total. Nickel (830): 447 dissolved and 383 total.

Table 3-1

Total Surface Water Copper Concentrations (µg/L) in South San Francisco Bay, 1989 – 1999

Station	N =	Minimum	Maximum	Mean	Median	SD	Dates
PA+STATION1	14	3.4	9.9	5.8	4.9	2.1	09/07/89 - 02/19/92
PA+STATION2	14	4.1	11.0	5.8	5.0	1.9	09/07/89 - 02/19/92
PA+STATION3	12	4.9	16.0	8.1	6.6	3.3	09/07/89 - 02/13/92
PA+STATION4	12	3.8	9.6	5.5	4.8	1.9	09/07/89 - 02/13/92
SBDA+C-1-0	21	3.2	7.5	5.3	5.4	1.2	09/06/89 - 02/17/92
SBDA+C-1-1	19	2.3	8.6	5.2	5.3	1.7	09/06/89 - 02/17/92
SBDA+C-1-3	20	4.9	25.6	13.3	14.3	7.0	09/06/89 - 02/17/92
SBDA+C-2-0	12	2.4	30.0	6.8	4.4	7.5	09/06/89 - 02/11/92
SBDA+C-2-5	13	4.8	18.2	8.8	6.0	4.7	09/06/89 - 02/11/92
SBDA+C-3-0	18	4.9	22.1	10.1	7.1	5.6	09/06/89 - 02/17/92
SBDA+C-5-0	12	4.3	14.0	7.4	6.6	3.0	09/06/89 - 02/11/92
SBDA+C-6-0	16	4.1	16.0	8.6	8.0	3.6	09/06/89 - 02/11/92
SBDA+C-X	12	6.0	18.2	12.1	12.0	3.6	09/06/89 - 02/11/92
SBDA+R-2	13	5.1	16.0	8.5	6.6	3.5	09/06/89 - 02/11/92
SBDA+R-4	18	5.2	23.0	10.6	9.3	5.0	09/06/89 - 02/17/92
SBDA+R-5	15	5.2	17.0	8.4	8.5	3.0	09/06/89 - 02/11/92
SBDA+SB-4	13	3.4	9.6	5.4	4.7	1.8	09/06/89 - 02/11/92
SBDA+SB-5	18	3.4	9.1	5.2	4.6	1.8	09/06/89 - 02/17/92
SBDA+SB-6	12	3.8	12.0	6.1	5.4	2.3	09/06/89 - 02/11/92
SBDA+SB-7	18	3.4	10.0	5.3	5.2	1.5	09/06/89 - 02/17/92
RMP+BA10	12	3.1	11.8	5.9	5.6	2.4	01/31/94 - 07/29/97
RMP+BA20	15	3.0	6.3	4.5	4.5	1.0	03/02/93 - 07/28/97
RMP+BA30	15	3.0	7.2	4.3	3.9	1.2	03/02/93 - 07/28/97
RMP+C-1-3	12	3.5	14.4	7.0	6.7	3.1	01/31/94 – 07/29/97
RMP+C-3-0	12	4.2	13.0	8.5	8.2	3.4	01/31/94 – 07/29/97
SJ+CC	25	3.1	13.1	6.9	6.6	2.7	01/12/96 - 03/12/97
SJ+DBN	25	2.4	11.3	4.3	4.0	1.9	01/12/96 - 03/12/97
SJ+DBS	25	2.7	13.5	4.8	4.1	2.1	01/12/96 - 03/12/97
SB01	37	2.1	13.4	5.1	4.6	2.2	02/06/97 - 03/09/99
SB02	37	2.6	15.5	6.0	6.1	2.2	02/18/97 - 03/09/99
SB03	38	3.5	107.3	17.5	7.7	22.1	02/06/97 - 03/09/99
SB04	42	4.7	25.4	9.9	8.6	4.3	02/06/97 - 03/09/99
SB05	41	3.7	67.3	15.4	10.0	16.5	02/06/97 - 03/09/99
SB06	39	2.8	34.3	8.1	7.0	5.7	02/18/97 - 03/09/99
SB07	39	3.6	42.8	11.6	8.3	9.2	02/06/97 - 03/09/99
SB08	39	2.8	16.2	8.3	7.6	3.8	02/06/97 - 03/09/99
SB09	36	3.0	12.6	6.0	5.6	2.3	02/06/97 - 03/09/99
SB10	35	2.3	33.2	8.1	5.9	6.1	02/18/97 - 02/16/99
SB11	26	3.1	44.3	7.3	4.9	8.2	08/18/97 - 02/16/99
SB12	28	2.2	23.6	9.3	6.9	6.4	09/02/97 - 02/16/99

Table 3-2
Dissolved Surface Water Copper Concentrations (µg/L) in South San Francisco Bay, 1989 – 1999

Station	N =	Minimum	Maximum	Mean	Median	SD	Dates
PA+STATION1	14	1.4	6.3	3.4	3.2	1.2	09/07/89 - 02/19/92
PA+STATION2	14	1.7	6.8	4.0	4.1	1.6	09/07/89 - 02/19/92
PA+STATION3	12	2.3	16.0	6.1	5.3	3.5	09/07/89 - 02/13/92
PA+STATION4	12	1.3	7.6	4.2	3.9	1.6	09/07/89 - 02/13/92
SBDA+C-1-0	21	2.9	6.4	4.4	4.4	0.9	09/06/89 - 02/17/92
SBDA+C-1-1	19	1.4	6.5	3.1	3.2	1.4	09/06/89 - 02/17/92
SBDA+C-1-3	20	2.5	8.9	4.3	3.6	2.0	09/06/89 - 02/17/92
SBDA+C-2-0	12	1.4	6.7	3.1	2.9	1.6	09/06/89 - 02/11/92
SBDA+C-2-5	13	3.1	6.8	4.3	4.1	1.0	09/06/89 – 02/11/92
SBDA+C-3-0	18	2.5	9.4	4.2	3.7	1.7	09/06/89 – 02/17/92
SBDA+C-5-0	12	3.0	7.3	4.2	3.8	1.4	09/06/89 - 02/11/92
SBDA+C-6-0	16	3.0	7.9	4.0	3.6	1.3	09/06/89 - 02/11/92
SBDA+C-X	12	3.5	7.3	4.5	4.2	1.1	09/06/89 - 02/11/92
SBDA+R-2	13	2.7	7.4	4.0	3.6	1.2	09/06/89 - 02/11/92
SBDA+R-4	18	2.6	6.8	3.9	3.7	1.2	09/06/89 – 02/17/92
SBDA+R-5	15	2.3	7.6	4.2	3.8	1.5	09/06/89 - 02/11/92
SBDA+SB-4	13	1.4	6.3	3.4	3.1	1.1	09/06/89 - 02/11/92
SBDA+SB-5	18	2.2	6.5	3.5	3.2	1.0	09/06/89 - 02/17/92
SBDA+SB-6	12	2.2	7.0	3.9	3.6	1.3	09/06/89 - 02/11/92
SBDA+SB-7	18	2.3	6.6	3.7	3.5	1.1	09/06/89 - 02/17/92
RMP+BA10	12	1.6	4.9	3.4	3.2	1.0	01/31/94 - 07/29/97
RMP+BA20	15	1.8	5.0	3.1	3.0	0.9	03/02/93 - 07/28/97
RMP+BA30	15	1.9	3.7	2.8	2.8	0.6	03/02/93 - 07/28/97
RMP+C-1-3	12	1.4	4.8	2.8	2.5	1.2	01/31/94 – 07/29/97
RMP+C-3-0	12	1.6	5.9	3.4	3.4	1.2	01/31/94 – 07/29/97
SJ+CC	25	2.0	4.1	3.1	3.0	0.6	01/12/96 - 03/12/97
SJ+DBN	25	1.4	3.7	2.5	2.5	0.6	01/12/96 - 03/12/97
SJ+DBS	25	1.7	3.7	2.7	2.7	0.5	01/12/96 - 03/12/97
SB01	41	1.4	3.6	2.5	2.6	0.7	02/06/97 - 03/09/99
SB02	38	1.5	4.2	2.6	2.6	0.7	02/18/97 - 03/09/99
SB03	38	1.3	4.1	2.8	2.9	0.8	02/06/97 - 03/09/99
SB04	37	1.6	4.3	2.8	2.7	0.8	02/06/97 - 03/09/99
SB05	39	1.5	3.9	2.8	2.9	0.8	02/06/97 - 03/09/99
SB06	38	1.5	4.3	2.8	2.9	0.8	02/18/97 - 03/09/99
SB07	39	1.5	4.1	2.9	2.9	0.7	02/06/97 - 03/09/99
SB08	41	1.5	4.4	2.8	3.0	0.7	02/06/97 - 03/09/99
SB09	41	1.5	4.2	2.8	3.0	0.7	02/06/97 - 03/09/99
SB10	42	1.6	4.6	3.0	3.2	0.8	02/18/97 - 02/16/99
SB11	27	1.0	3.4	1.9	1.7	0.7	08/18/97 - 02/16/99
SB12	28	0.9	4.4	1.6	1.5	0.7	09/02/97 - 02/16/99

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Table 3-3

Total Surface Water Nickel Concentrations (μg/L) in South San Francisco Bay, 1989 – 1999

Station	N =	Minimum	Maximum	Mean	Median	SD	Dates
PA+STATION1	14	3.7	22.0	7.8	6.2	5.0	09/07/89 - 02/19/92
PA+STATION2	14	4.4	12.2	6.9	6.3	2.2	09/07/89 - 02/19/92
PA+STATION3	12	4.3	9.4	6.4	5.9	1.9	09/07/89 - 02/13/92
PA+STATION4	12	4.2	12.0	6.2	5.5	2.2	09/07/89 - 02/13/92
SBDA+C-1-0	21	8.8	25.0	13.6	13.0	3.7	09/06/89 - 02/17/92
SBDA+C-1-1	19	6.2	15.3	10.9	11.0	2.4	09/06/89 - 02/17/92
SBDA+C-1-3	20	7.2	48.0	22.1	21.0	12.1	09/06/89 - 02/17/92
SBDA+C-2-0	12	6.4	58.0	15.0	10.7	14.0	09/06/89 - 02/11/92
SBDA+C-2-5	13	10.0	28.0	17.9	16.0	6.4	09/06/89 – 02/11/92
SBDA+C-3-0	18	10.0	38.0	17.8	17.0	8.2	09/06/89 - 02/17/92
SBDA+C-5-0	12	5.9	23.0	12.3	10.8	4.9	09/06/89 - 02/11/92
SBDA+C-6-0	16	6.1	24.2	13.9	13.5	6.3	09/06/89 - 02/11/92
SBDA+C-X	12	13.0	32.0	23.5	23.3	5.7	09/06/89 - 02/11/92
SBDA+R-2	13	6.9	27.0	14.3	12.8	6.6	09/06/89 - 02/11/92
SBDA+R-4	18	7.6	40.0	18.1	18.5	8.0	09/06/89 – 02/17/92
SBDA+R-5	15	8.1	23.0	14.6	13.0	5.4	09/06/89 - 02/11/92
SBDA+SB-4	13	3.7	15.1	6.5	5.6	3.1	09/06/89 - 02/11/92
SBDA+SB-5	18	4.1	22.5	8.2	6.8	4.4	09/06/89 - 02/17/92
SBDA+SB-6	12	4.4	16.0	9.4	8.1	3.9	09/06/89 - 02/11/92
SBDA+SB-7	18	4.3	13.0	8.3	8.1	2.6	09/06/89 - 02/17/92
RMP+BA10	12	4.2	22.3	10.2	8.7	5.0	01/31/94 – 07/29/97
RMP+BA20	15	4.0	10.7	6.5	6.3	1.9	03/02/93 – 07/28/97
RMP+BA30	15	3.6	13.0	6.0	4.6	2.6	03/02/93 - 07/28/97
RMP+C-1-3	12	6.1	36.7	14.6	11.3	8.4	01/31/94 – 07/29/97
RMP+C-3-0	12	4.0	36.0	17.2	16.2	8.7	01/31/94 – 07/29/97
SJ+CC	25	4.5	22.3	10.8	8.9	5.3	01/12/96 - 03/12/97
SJ+DBN	25	2.7	18.4	5.4	4.3	3.1	01/12/96 – 03/12/97
SJ+DBS	25	2.9	22.8	6.5	5.8	3.8	01/12/96 - 03/12/97
SB01	30	3.0	23.5	8.0	6.9	4.4	02/06/97 - 03/09/99
SB02	27	2.4	33.0	10.1	9.4	5.4	02/18/97 - 03/09/99
SB03	34	2.7	211.3	34.0	13.4	46.6	02/06/97 - 03/09/99
SB04	36	4.5	36.8	20.7	18.5	8.1	02/06/97 - 03/09/99
SB05	36	3.0	133.3	30.8	33.0	33.0	02/06/97 - 03/09/99
SB06	32	2.5	63.0	14.9	10.7	12.7	02/18/97 - 03/09/99
SB07	38	3.1	89.0	23.5	15.8	19.5	02/06/97 - 03/09/99
SB08	36	4.0	33.3	14.7	12.5	8.1	02/06/97 - 03/09/99
SB09	33	4.4	23.2	10.1	8.5	4.7	02/06/97 - 03/09/99
SB10	32	3.9	71.6	14.8	10.3	13.2	02/18/97 - 02/16/99
SB11	24	5.0	103.0	17.6	10.4	20.8	08/18/97 - 02/16/99
SB12	25	5.8	53.8	21.1	14.8	13.2	09/02/97 – 02/16/99

Table 3-4
Dissolved Surface Water Nickel Concentrations (µg/L) in South San Francisco Bay, 1989 – 1999

Station	N =	Minimum	Maximum	Mean	Median	SD	Dates
PA+STATION1	14	1.6	5.1	3.2	2.7	1.1	09/07/89 – 02/19/92
PA+STATION2	14	2.0	5.2	3.6	3.6	1.0	09/07/89 – 02/19/92
PA+STATION3	12	2.7	6.9	4.4	4.1	1.3	09/07/89 – 02/13/92
PA+STATION4	12	1.6	5.5	4.0	4.2	1.2	09/07/89 – 02/13/92
SBDA+C-1-0	21	6.2	26.0	11.1	10.0	4.2	09/06/89 – 02/17/92
SBDA+C-1-1	19	2.7	9.5	5.8	5.6	2.1	09/06/89 – 02/17/92
SBDA+C-1-3	20	3.9	8.9	6.3	5.4	1.8	09/06/89 – 02/17/92
SBDA+C-2-0	12	4.0	11.0	6.6	6.2	2.0	09/06/89 – 02/11/92
SBDA+C-2-5	13	4.4	15.0	8.4	8.6	3.3	09/06/89 – 02/11/92
SBDA+C-3-0	18	3.3	11.0	6.2	5.9	2.3	09/06/89 – 02/17/92
SBDA+C-5-0	12	3.3	9.3	5.6	5.2	1.9	09/06/89 – 02/11/92
SBDA+C-6-0	16	2.7	8.9	5.2	5.1	1.8	09/06/89 – 02/11/92
SBDA+C-X	12	3.5	12.0	7.3	7.0	3.1	09/06/89 – 02/11/92
SBDA+R-2	13	2.9	9.2	5.4	4.5	2.1	09/06/89 – 02/11/92
SBDA+R-4	18	2.8	9.0	5.1	4.8	1.8	09/06/89 – 02/17/92
SBDA+R-5	15	3.0	9.1	5.3	5.0	2.1	09/06/89 – 02/11/92
SBDA+SB-4	13	1.6	5.1	3.1	2.7	1.1	09/06/89 – 02/11/92
SBDA+SB-5	18	2.3	9.2	4.0	3.6	1.6	09/06/89 – 02/17/92
SBDA+SB-6	12	2.4	11.8	5.5	4.8	3.0	09/06/89 – 02/11/92
SBDA+SB-7	18	1.6	10.6	4.6	4.3	1.9	09/06/89 - 02/17/92
RMP+BA10	12	2.1	6.6	4.1	4.0	1.1	01/31/94 - 07/29/97
RMP+BA20	15	2.4	4.4	3.2	3.1	0.6	03/02/93 – 07/28/97
RMP+BA30	15	2.3	3.4	2.9	2.9	0.3	03/02/93 – 07/28/97
RMP+C-1-3	12	1.6	7.0	4.3	3.9	1.7	01/31/94 – 07/29/97
RMP+C-3-0	12	2.8	10.9	6.8	6.7	2.1	01/31/94 – 07/29/97
SJ+CC	25	2.0	4.5	3.2	3.2	0.6	01/12/96 - 03/12/97
SJ+DBN	25	1.7	3.7	2.4	2.3	0.5	01/12/96 – 03/12/97
SJ+DBS	25	1.8	3.7	2.6	2.6	0.5	01/12/96 - 03/12/97
SB01	39	1.5	3.8	2.7	2.7	0.6	02/06/97 - 03/09/99
SB02	39	1.6	5.3	3.0	3.0	8.0	02/18/97 – 03/09/99
SB03	38	1.8	6.5	3.7	3.5	1.0	02/06/97 - 03/09/99
SB04	41	2.6	13.4	5.9	5.5	2.0	02/06/97 - 03/09/99
SB05	40	1.7	7.4	4.4	4.1	1.5	02/06/97 - 03/09/99
SB06	40	1.6	6.6	3.5	3.2	1.1	02/18/97 – 03/09/99
SB07	39	2.3	10.1	4.3	4.0	1.6	02/06/97 - 03/09/99
SB08	41	1.7	5.3	3.4	3.2	8.0	02/06/97 - 03/09/99
SB09	41	1.7	5.7	3.2	3.1	8.0	02/06/97 - 03/09/99
SB10	38	2.0	5.4	3.4	3.5	0.7	02/18/97 – 02/16/99
SB11	25	2.3	8.6	3.8	3.0	1.8	08/18/97 – 02/16/99
SB12	26	1.8	6.9	3.8	3.6	1.1	09/02/97 – 02/16/99

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As part of the overall effort to address uncertainty associated with the impairment assessment, the variability of the copper and nickel measurements in the water column was investigated. The focus of these investigations was on the recent SJSB measurements, which were numerous, replicated and frequently collected. The first measure of uncertainty is in the laboratory variability. The coefficient of variation [(standard deviation / mean) x 100%] for the replicate samples for both copper and nickel, total and dissolved averaged less than 10%. The coefficients of variation (CV) at individual stations over the two-year sampling interval were also relatively small, with dissolved copper and nickel CVs exhibiting lower variability than CVs that were based on total copper and nickel concentrations. The ranges for the eight stations within the main water mass of Lower South San Francisco Bay were:

Total copper 22 - 126%

Dissolved copper 19 – 57 %

Total nickel 30 - 137%

Dissolved nickel 10 – 38%

The relatively low variability observed in these data can also be seen in the cumulative distribution plots for dissolved copper concentrations measured at four stations (Figure 3-5). In each location the range of values is relatively small. One of the explanations for the observed variability is seasonal change in copper and nickel concentrations. In Figure 3-6 the dissolved copper concentrations measured at selected SJSB, RMP and SBDA stations are shown as well as the stream flow measured at a gauging station on the Guadalupe River. The measured concentrations are highest in the dry season, and it appears that they are affected by hydrologic factors.

The two largest sources of total copper and nickel to the Lower South San Francisco Bay are sediment exchange during resuspension and nonpoint source loads from tributaries. Most of the tributary loads occur during the wet season. Resuspension is highest during the windy spring and summer months, but also occurs during the rest of the year during periods of high winds or currents. During the dry season, the relative contributions of the POTW loads are higher than during the wet season since tributary nonpoint source loads become small.

Point sources are major contributors of dissolved copper and nickel, since nonpoint sources are believed to contribute primarily particulate loads. Internal cycling processes are also important components of the dissolved copper and nickel loads, particularly during the dry season. Mass balance calculations show that during the dry season, internal cycling fluxes occur that are similar in magnitude to the dissolved copper and nickel fluxes from the POTW discharges (See Appendix B in Conceptual Model Report 1999). These are the two largest sources of dissolved metals to the water column during this season. The specific processes causing the internal cycling fluxes cannot be identified with the available data, but they could include net desorption of metals during sediment resuspension, decomposition of algal detritus in the sediments, and solubilization of metals in phytoplankton during feeding by benthic bivalves. During the wet season, the mass balance calculations indicate that internal cycling processes result in a net sink of dissolved copper and nickel from the water. Again, the specific processes cannot be identified

with the available data, but they could include net adsorption of metals on suspended solids entering the South Bay from tributary inflows and uptake by phytoplankton during the spring blooms. The magnitudes of the internal cycling fluxes are similar during both seasons, but they represent a dissolved source during the dry season and a dissolved sink during the wet season. The estimated cycling fluxes have high uncertainties cue to the existing data limitations and simplifying assumptions required in the analyses.

Copper and nickel loads from sediment diffusion and atmospheric deposition appear to be relatively small and together represent only a few percent of the total loads.

### 3.2 Sediments

Copper and nickel sediment concentrations have been collected from the top 5 cm of sediments throughout the San Francisco Bay by the Regional Monitoring Program (RMP) and are shown in Figure 3-7. Selected statistics of the data are provided in Table 3-5.

Average surface sediment copper concentrations reported by the RMP between 1994 and 1997 for the entire San Francisco Bay ranged from approximately 20 to 60 mg/kg (dry weight) (n = 138 samples), with the minimum and maximum copper concentrations being 7.2 and 94.6 mg/kg, respectively. The average surface sediment copper concentrations for the two Lower South San Francisco Bay main water body sites was 41.0 mg/kg (dry weight), with the minimum and maximum copper concentrations ranging from 24.5 to 55.6 mg/kg.

Average surface sediment nickel concentrations reported by the RMP between 1994 and 1997 for the entire San Francisco Bay ranged from approximately 65 to 110 mg/kg (dry weight) (n = 138 samples), with the minimum and maximum nickel concentrations being 45.1 and 129.8 mg/kg, respectively. The average surface sediment nickel concentrations for the two Lower South San Francisco Bay main water body sites was 92.1 mg/kg (dry weight), with the minimum and maximum nickel concentrations ranging from 70.3 to 117.9 mg/kg.

In contrast to the water column copper and nickel concentrations, sediment copper and nickel concentrations are more uniform throughout the Bay. Concentrations in central South San Francisco Bay are somewhat lower than elsewhere, as they were for water column concentrations. The sediment concentrations at each location are relatively constant, as noted by the small standard deviations of the data (Table 3-5).

There are three sediment core data sets available for the South San Francisco Bay area (one core collected one km south of the San Mateo Bridge; one core collected from Coyote Creek; and one core collected from Mayfield Slough). The data from these three cores were compiled and compared to a sediment core (Core #93-1) collected from Tomales Bay, California (a location with minimal anthropogenic impact). These data have been plotted and are presented in Figure 3-8. The Tomales Bay core results portray a fairly constant concentration ( $20 \mu g/g$ ) over depth, with a slight enrichment in the top 50 cm. Copper concentrations near the San Mateo Bridge are higher at all depths, and also show enriched in concentrations in the top 50 cm. In contrast, sediment nickel concentrations are uniformly

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Table 3-5
Selected Statistics of Sediment Copper and Nickel Concentrations (μg/g-dry weight) in Surface Sediments at Locations Throughout San Francisco Bay

	Sample						Standard
Station	Size	Minimum	Maximum	Mean	Median	UCL <sub>95</sub> *	Deviation
Sediment Copper	•						
SFEI+BA10	4	24.5	48.9	36.4	36.0	49.1	10.8
SFEI+BA21	6	38.3	55.6	45.6	42.7	51.8	7.5
SFEI+BA30	6	37.3	48.1	43.0	44.0	47.0	4.9
SFEI+BA41	6	35.4	54.9	43.1	40.4	48.9	7.2
SFEI+BB15	6	27.3	37.6	31.6	31.6	34.6	3.6
SFEI+BB30	6	33.2	46.2	37.9	37.1	41.7	4.6
SFEI+BB70	6	36	48.1	41.8	41.8	45.2	4.1
SFEI+BC11	6	25.1	47.7	36.1	35.9	43.2	8.6
SFEI+BC21	6	16.1	38.4	26.5	27.9	33.5	8.6
SFEI+BC32	6	31.1	38.9	33.9	33.7	36.3	2.8
SFEI+BC41	6	36.4	46.9	40.7	39.6	43.9	3.9
SFEI+BC60	6	7.2	11.1	9.1	8.9	10.3	1.5
SFEI+BD15s	4	49.6	66.7	55.7	53.3	64.9	7.8
SFEI+BD22	6	41	54.1	47.9	47.5	52.0	4.9
SFEI+BD31	6	35	70.6	53.5	55.8	64.4	13.2
SFEI+BD31	6	17.2	27.3	20.5	19.4	23.7	3.9
SFEI+BD50	6	43.2	68.3	59.9	61.5	67.6	9.4
SFEI+BF10	6	14.6	25.6	19.9	19.7	23.9	4.7
SFEI+BF21	4	39.8	67.1	57.2	60.9	71.3	11.9
SFEI+BF40	6	45.3	71.9	61.5	65.8	71.3	10.7
SFEI+BG20	6	45.3 20.7	42.3	28.2	25.2	70.3 35.2	8.5
SFEI+BG30		30.7		26.2 38.1	25.2 37.6	42.9	5.7
	6		47.5				
SFEI+C-1-3	6	22.7	94.6	39.9	31.4	62.3	27.2
SFEI+C-3-0	6	21.1	57.8	36.7	34.8	50.3	16.6
Sediment Nickel							
SFEI+BA10	4	72.3	116.1	91.8	89.5	114.8	19.5
SFEI+BA21	6	70.3	117.9	92.4	91.5	105.8	16.3
SFEI+BA30	6	48.4	103.0	83.3	84.1	99.9	20.2
SFEI+BA41	6	65.8	103.9	82.1	80.3	93.3	13.6
SFEI+BB15	6	45.1	76.7	66.4	68.8	75.6	11.2
SFEI+BB30	6	69.3	101.1	81.5	81	91.4	12.0
SFEI+BB70	6	63.9	98.2	82.4	81.7	91.8	11.5
SFEI+BC11	6	47.5	85.4	68.6	71.8	82.2	16.6
SFEI+BC21	6	55.9	79.4	65.9	63.5	74.0	9.8
SFEI+BC32	6	64.7	81.1	72.3	73.1	77.7	6.5
SFEI+BC41	6	73.1	91.9	82.5	82.1	87.8	6.4
SFEI+BC60	6	59.1	73.8	65.7	64.7	69.8	4.9
SFEI+BD15s	4	93.6	129.7	110.8	109.9	129.2	15.7
SFEI+BD22	6	67.4	97.6	81.8	78.7	90.9	11.0
SFEI+BD31	6	82.9	117.5	99.3	100.1	111.4	14.8
SFEI+BD41	6	61.9	80	73.0	73.5	78.3	6.4
_							
SFEI+BD50	6	76.5 71.9	116.9 92.3	98.3 80.7	100.1 78.4	110.2 87.7	14.4 8.6
SFEI+BF10	6						
SFEI+BF21	4	68.3	115.4	97.8	103.8	123.9	22.2
SFEI+BF40	6	85.8	124.6	106.3	107.4	117.9	14.1
SFEI+BG20	6	83.1	113.2	96.2	95.0	106.0	11.9
SFEI+BG30	6	52.6	79.2	65.9	64.7	74.6	10.6
SFEI+C-1-3	6	57.9	130.8	81.4	77.4	102.7	25.9
SFEI+C-3-0	6	68.6	129.8	100.1	102.6	119.3	23.4

<sup>\*</sup> UCL95 = 95<sup>th</sup> percent upper confidence level of mean.

higher in the Tomales Bay core than in the South Bay and Mayfield Slough cores and approximately equal to the concentrations of nickel found in the Coyote Creek core (Conceptual Model Report, 1999). One possible explanation for this could be due to the different geologic formations at the two locations. Nickel is strongly enriched in some geologic components of the watershed as evidenced from sediment cores collected in the North San Francisco Bay that indicated that concentrations of nickel reported in surface sediments were originated from natural geologic outputs (Hornberger, et al. In: Luoma, et al 1998) and most likely originated from mobile nickel deposits in ultramafic rocks in the region (Hornberger et al. In: Luoma, et al 1995).

In the lower graph in Figure 3-8, profiles of copper and nickel are shown at two locations in the Lower South San Francisco Bay: Mayfield Slough and Coyote Creek. The profiles of copper are similar at the two locations, but the same is not true for nickel where for most of the depth profile, nickel concentrations are higher in Coyote Creek. Note that the Tomales Bay nickel core sample concentrations are higher than, or approximately equal to, nickel concentrations at both South San Francisco Bay locations.

One possible explanation for this could be due to the different geologic formations at the two locations. Nickel is strongly enriched in some geologic components of the watershed as evidenced from sediment cores collected in North San Francisco Bay that indicated that concentrations of nickel reported in surficial sediments were derived from natural geologic outputs Hornberger et al (In: Luoma, et al (1998)) and most likely originated from mobile nickel deposits in ultramafic rocks in the region (Hornberger et al In: Luoma et al 1995).

In the lower graph in Figure 3-8, profiles of copper and nickel are shown at two locations in Lower South San Francisco Bay: Mayfield Slough and Coyote Creek. The profiles of copper are similar at the two locations, but the same is not true for nickel, where for most of the depth profile nickel concentrations are higher in Coyote Creek. Note that the Tomales Bay nickel core sample concentrations are higher than, or approximately equal to, nickel concentrations at both South San Francisco Bay locations.

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# 3.3 Ambient Toxicity in Lower South San Francisco Bay

Ambient toxicity is frequently monitored in the lower South San Francisco Bay. The results from seven separate ambient toxicity studies were used in this assessment of ambient toxicity in the lower South San Francisco Bay:

St	udy	Sampling Period	Sample Frequency
1.	Palo Alto Clam Study (Luoma et al., 1998;		
	Hornberger et al, 1998)	1977–1997	"Near Monthly"
2.	Cities of San Jose/Sunnyvale		
	E5E/NPDES Studies		
	(Larry Walker Associates, 1991a, b)	9/89–9/90	Monthly
3.	Development of Site-Specific Criteria		
	for Copper for San Francisco Bay		
	(S.R. Hansen & Associates, 1992a)	5/91–10/91	Monthly
4.	Development of Site-Specific Criteria		
	for Nickel for San Francisco Bay		
	(S.R. Hansen & Associates, 1992b)	9/91–10/91	Monthly
5.	Regional Monitoring Program (RMP)	1993–1997	Quarterly
6.	Bay Protection and Toxic Cleanup Program	9/94–12/97	Wet & Dry Seasons
7.	City of San Jose WER Study	1/96–3/97	Bi-weekly

Each of these studies has assessed ambient toxicity in the lower South San Francisco Bay using at least one of the following toxicity assessment methods:

- Water column toxicity bioassay
- Sediment bioassays (Whole sediment and pore-water)
- Bivalve tissue bioconcentration

The assessment of these results was separated into three sections. The first section addresses ambient water column toxicity, the second addresses ambient sediment toxicity, and the third addresses bivalve tissue bioconcentration.

#### 3.3.1 Ambient Water Column Toxicity

Ambient water column toxicity in the lower South San Francisco Bay is rarely observed. Over 150 water column bioassays have been performed on ambient lower South San Francisco Bay

waters since 1991. The results obtained from these bioassays have been previously reported (Larry Walker Associates et al., 1991 a, b; S.R. Hansen & Associates 1992 a, b; Regional Monitoring Program 1993 –1996; City of San Jose 1998). Of these tests, there have been only four reported incidents of ambient Lower South San Francisco Bay toxicity. These samples were collected in 1991 (S.R. Hansen & Associates 1992 a, b) and in July 1997 (Regional Monitoring Program) and both copper and nickel were excluded as possible causes of the observed toxicity. This was because:

## S.R. Hansen & Associates (1992a, b):

- The ambient concentrations of dissolved copper (1.3 μg/L) and nickel (3.0 and 3.6 μg/L) were much lower than the toxicity thresholds that were reported for dissolved copper and nickel for the two test species (*T. pseudonana* and *Lytechinus pyctus*, respectively) and
- Ambient site-water "controls" exhibited toxicity while ambient site-water that was spiked with increasing concentrations of copper or nickel were not toxic. This indicates that there was some type of anomalous response in the "control" treatment that was not observed in any of the metal spiked treatments (possibly caused by sample contamination and/or stressed test organisms in the "control" treatment that was absent from any of the metal-spiked treatments). In other words, if the test organisms were on the response curve for either copper or nickel (i.e., site-water toxicity), then any addition of copper or nickel to the site-water test solution would only serve to exacerbate the toxic effect. Since only the site-water controls exhibited toxicity and the site-water that was spiked with metal failed to cause toxicity, then copper and nickel can be safely excluded as causes of toxicity.

#### RMP (1997) Monitoring Effort:

• The published species mean acute values (SMAVs) for *M. edulis* for copper and nickel are 9.6 μg/L and 891 μg/L, respectively; the published acute values for *Americamysis bahia* (*Mysidopsis bahia*) for copper and nickel are 157 μg/L and 508 μg/L, respectively. The ambient dissolved copper and nickel concentrations measured from Redwood Creek south to Guadalupe River in July 1997 ranged from 1.2 to 3.9 μg/L and 2.1 to 9 μg/L, respectively. The low ambient copper and nickel concentrations compared to the SMAVs, and the fact that *M. edulis*, which is 15 times more sensitive to copper than *A. bahia*, did not exhibit toxicity during the same sampling period, strongly suggests that the observed toxicity to *A. bahia* was not caused by either copper or nickel.

The early life-stage of the most sensitive test organisms that were reported in the national dataset were used as the biological detectors for these tests. Most aquatic toxicologists agree that it is during the early life-stage when the organisms are most sensitive to toxicants. The test organisms and endpoints used in these tests were:

- Mytilus edulis (mussel) embryo development,
- Crassostrea gigas (oyster) embryo development;

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- Lytichinus pyctus (urchin) embryo development;
- Thalassiosira pseudonana (diatom) cell growth;
- Menidia beryllina (minnow) survival and growth;
- Menidia menidia (minnow) survival and growth;
- *Americamysis bahia* (formerly, *Mysidopsis bahia*) mysid shrimp survival, growth, and fecundity.

# 3.3.2 Ambient Sediment Toxicity

Copper concentrations are elevated in Lower South San Francisco Bay sediments relative to background concentrations. Average surficial sediment copper concentrations in the Lower South San Francisco Bay are 41 mg/kg, approximately twice the average background concentration of 20 mg/kg. Nickel concentrations in the Lower South San Francisco Bay sediments (92 mg/kg) are not greater than those found in the rest of San Francisco Bay and are even lower than concentrations reported for Tomales Bay sediments (Conceptual Model Report 1999). Even so, it is extremely difficult to demonstrate that copper and nickel are the causes of any observed sediment toxicity occurring in the Lower South San Francisco Bay.

The Lower South San Francisco Bay sediments are routinely monitored for toxicity to aquatic organisms (both benthic and planktonic). The most comprehensive source of sediment monitoring data comes from the San Francisco Regional Monitoring Program (RMP). The RMP has monitored Lower South San Francisco Bay sediments for toxicity twice annually since 1993. They have determined that the Lower South San Francisco Bay sediments are fairly consistently toxic to the amphipod, *Eohaustorius estuarius*, with their "South Bay" site exhibiting toxicity in 63% of the toxicity tests performed. However, they report no observed toxicity occurring in porewater collected from the same sediments and using *M. edulis* embryos as the bioassay organisms. Other studies (Larry Walker Associates 1991a, b; Bay Protection and Toxic Cleanup Program, 1998) indicate that Lower South San Francisco Bay sediments were not toxic to aquatic organisms.

There are currently no definitive methods that can be used to determine whether any observed sediment toxicity is caused by the presence of copper. Sediments are extremely complex and even though many of the components that make up the sediment are fairly well known, any interactions between those components and copper remain unclear at this time.

#### 3.3.3 Bivalve Tissue Bioaccumulation

Three studies were used to assess bivalve tissue bioaccumulation (Larry Walker Associates et al., 1991 a, b; Regional Monitoring Program 1993 – 1996; USGS 1998 (Hornberger et al, 1998 and Luoma et al, 1998)). Lower South San Francisco Bay bivalve tissues have routinely been measured for the presence of elevated metals concentrations. All of these studies have reported tissue concentrations of copper and/or nickel that are elevated above ambient water column concentrations of those metals.

The RMP uses Accumulation Factors (AFs) to detect whether transplanted bivalves were accumulating (gaining) or depurating (losing) pollutants (e.g., copper and nickel). This value is

calculated as the quotient of the final and initial tissue pollutant concentrations (i.e., [tissue]<sub>final</sub>  $\div$  [tissue]<sub>initial</sub>). An AF = 1.0 indicates that there was no accumulation or loss of tissue pollutant concentration; AF values > 1.0 indicates accumulation; and AF < 1.0 indicates depuration. The summary results in Table 3-6 indicate that copper in the South Bay is more bioavailable to *C. gigas* than it is for *M. californianus* during both wet and dry seasons with AF values ranging from 2.0 to 11.8 for *C. gigas* and from 0.9 to 1.8 for *M. californianus*, with the greatest AF values for *C. gigas* occurring during the dry season. The AF values for South Bay nickel were mixed, with nickel being more bioavailable to *C. gigas* during the dry season (AF values range from 0.3 to 19) and more bioavailable to *M. californianus* during the wet season (AF values ranging from 0.5 to 8.6). It must be noted, however, that bioconcentrated copper and nickel in tissues is not an indicator of toxicity.

Table 3-6
Summary of bivalve tissue AF values for the 1995-1996 Bivalve Studies

Site	e Species		AF (Nickel)
Wet Seasons (1995 & 1996)			
Coyote Creek (BA10)	C. gigas	2.0	0.3
Dumbarton Br. (BA30)	M. californianus	0.9	0.5
Coyote Creek (BA10)	C. gigas	5.5	4.1
Dumbarton Br. (BA30)	M. californianus	1.6	8.6
Dry Seasons (1995 & 1996)			
Coyote Creek (BA10)	C. gigas	8.2	4.0
Dumbarton Br. (BA30)	M. californianus	1.4	3.2
Coyote Creek (BA10)	C. gigas	11.8	1.9
Dumbarton Br. (BA30)	M. californianus	1.8	1.8

However, Larry Walker Associates et al (1991 a, b) found that mussels transplanted to the lower South San Francisco Bay did not bioaccumulate copper and nickel in their tissues to any greater degree than had been reported by the State Mussel Watch Program for the entire San Francisco Bay. Indicating that copper and nickel were not more bioavailable in the Lower South San Francisco Bay than in the rest of San Francisco Bay. They examined the concentrations of copper and nickel in the tissues of resident bivalves (horse mussel, *Ischadium demissum*). The authors determined that there was no difference in copper and nickel tissue concentrations between *I. demissum* populations resident in the Lower South San Francisco Bay than for those that resided elsewhere in the Bay. In addition, they found no correlation between the proximity of the bivalve to a POTW outfall and concentrations of copper and nickel in tissues.

The USGS studies have directly established a linkage between elevated metal (copper and silver) concentrations in sediment, metal concentrations in bivalve tissues, and reduced bivalve reproductive capacity.

The USGS studies report that between the late 1970s and the late 1980s the clam population that occurred on a mudflat near the City of Palo Alto's POTW outfall was severely impacted by the

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presence of elevated concentrations of metals (e.g. copper and silver) in the local sediments. Average sediment dry weight copper concentrations have dropped significantly between 1977 and 1997, decreasing from 66.7 + 21.1 mg/kg between 1977 and 1981 to 45.1 + 8.7 mg/kg between 1992 and 1997 and ranging from 86 mg/kg (1979) to 43 mg/kg (1983) (Hornberger, et al., 1999). During approximately the same time period, average bivalve dry weight tissue copper concentrations were reduced by an order of magnitude; decreasing from 295 µg/g to 24 µg/g. Bivalve reproductive capability was closely associated with sediment and tissue copper concentrations, with less than 20% of the individual clams being reproductively active between 1974 and 1983. As sediment and tissue copper concentrations began to decrease, 70-100% of the clam population became reproductively active with reproductive patterns typical of less impacted sites not being observed until clam tissue copper concentrations reached 35 ppm. A comparison study (Luoma et al 1998) using clams collected from a mudflat near the San Jose POTW outfall has demonstrated clam tissue copper concentrations are similar to those currently observed at the Palo Alto POTW outfall. This study clearly demonstrates that this region in the Lower South San Francisco Bay (once highly impacted by copper) is no longer impacted by copper, when compared to the rest of San Francisco Bay.

## 3.4 Ambient Toxicity Conclusions

These studies, performed over the last eight years, indicate that, of the species tested for water column toxicity (i.e., *Crassostrea, Mytilus, Thalassiosira, Lytechinus* and *Menidia*), there was only one instance of water column toxicity to *Thalassiosira* and two of water column toxicity to *Lytechinus*. In all three cases, toxicity could not be attributed to either the presence of toxic concentrations of copper (*Thalassiosira*) or nickel (*Lytechinus*).

Neither copper nor nickel have been specifically isolated as the sediment components responsible for any observed toxicity occurring in the Lower South San Francisco Bay sediments. Sediments are complex. They contain many potential toxic chemicals that make it extremely difficult to isolate any single cause of toxicity. The sediment toxicity tests using either bivalves or amphipods indicated that there were several instances of sediment toxicity. The RMP study indicated that between 1993-1996, 60% of the sediment samples tested for the South Bay site (BA-21) were toxic to the amphipod, *Eohaustorius*. However, the studies performed by Larry Walker Associates (1991 a, b) indicated that South Bay sediments were no more toxic to *Eohaustorius* than were other sediments in San Francisco Bay.

Bivalve bioaccumulation studies performed by the RMP indicate that both copper and nickel were bioavailable to *Crassostrea* and *Mytilus* in the Lower South San Francisco Bay. Larry Walker Associates, et al (1991 a, b) indicated that any observed bioconcentration of copper and nickel in bivalve tissues was no greater in the Lower South San Francisco Bay than elsewhere in the Bay. The USGS studies (Hornberger, et al 1998; Luoma et al 1998) have shown a positive correlation between elevated sediment copper concentrations and elevated tissue concentrations. They also demonstrated that elevated tissue copper concentrations could be linked to reduced reproductive capacity in the clam. In addition, when sediment and clam tissue copper concentrations dropped, the clam resumed reproductive patterns observed in less impacted areas of the Bay. Thus, a site that was once heavily impacted by elevated sediment copper concentrations, is no longer impacted by sediment copper.



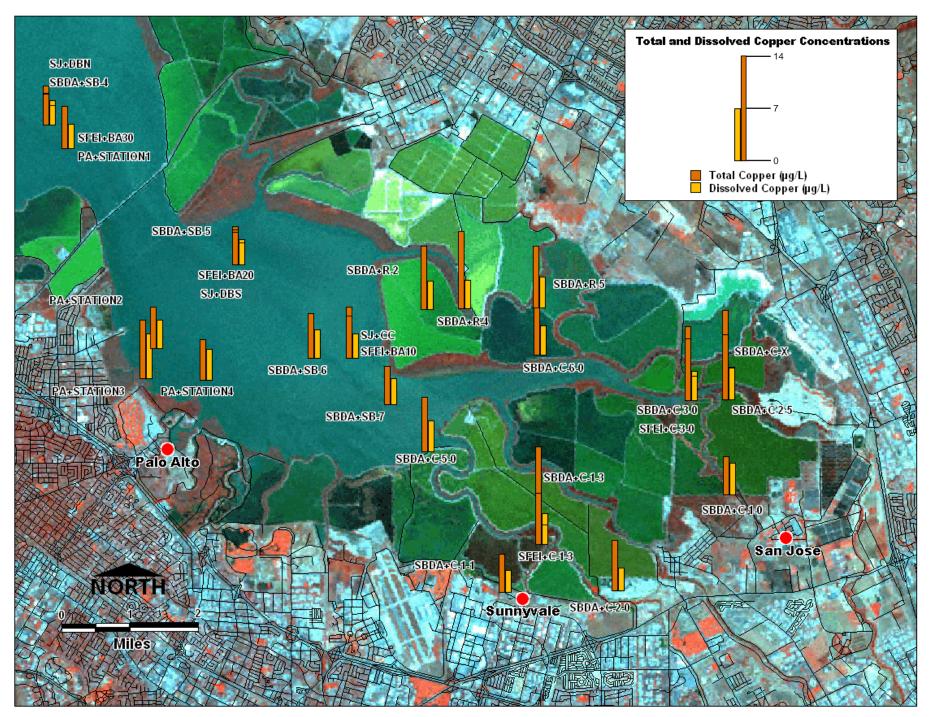


Figure 3-1. Average total and dissolved copper concentrations in water column at locations throughout Lower South San Francisco Bay.

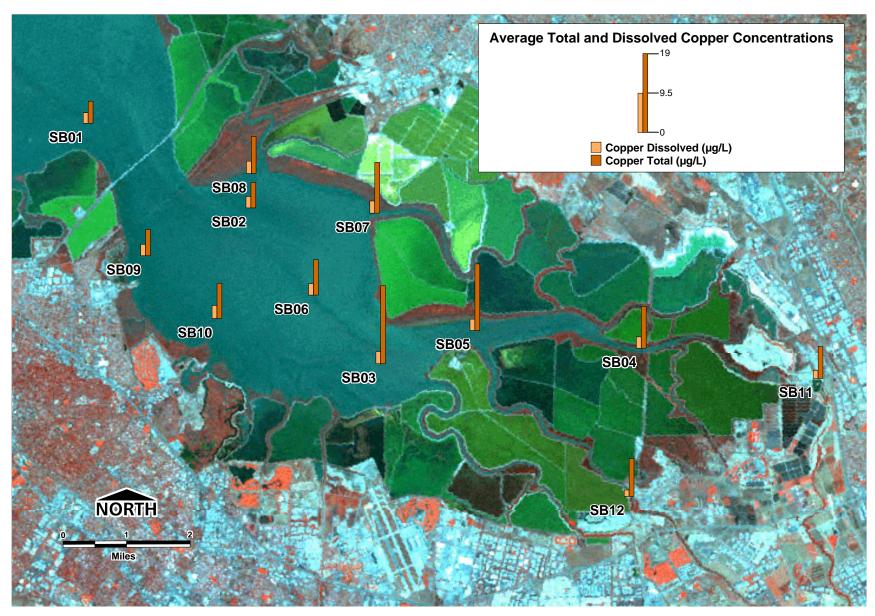


Figure 3-2. Average Total and Dissolved Copper Concentrations Reported in City of San Jose South Bay Monitoring Program.

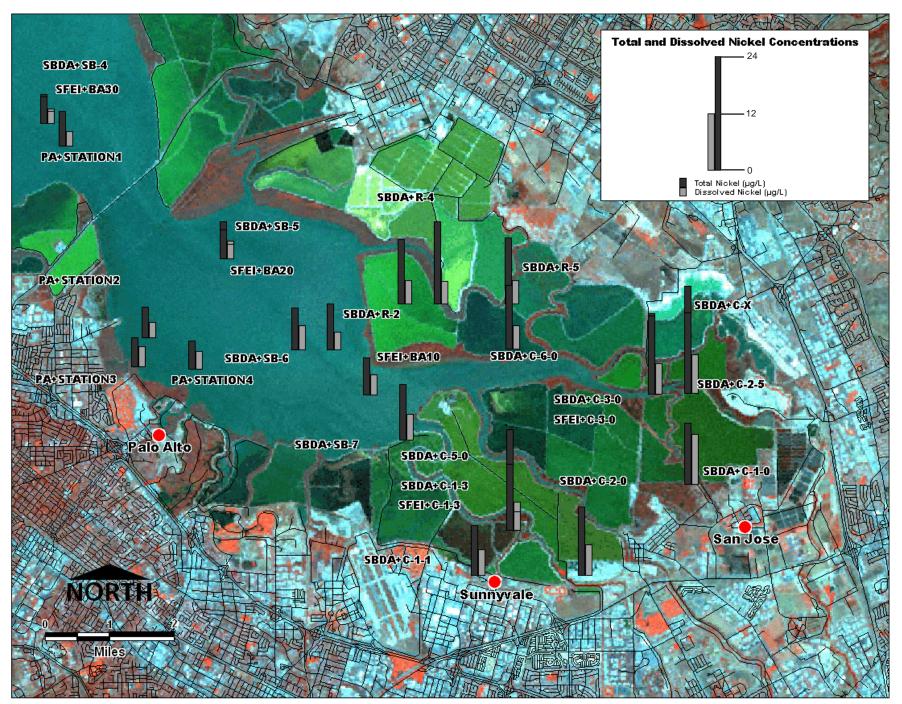


Figure 3-3. Average total and dissolved nickel concentrations in water column at locations throughout Lower South San Francisco Bay.

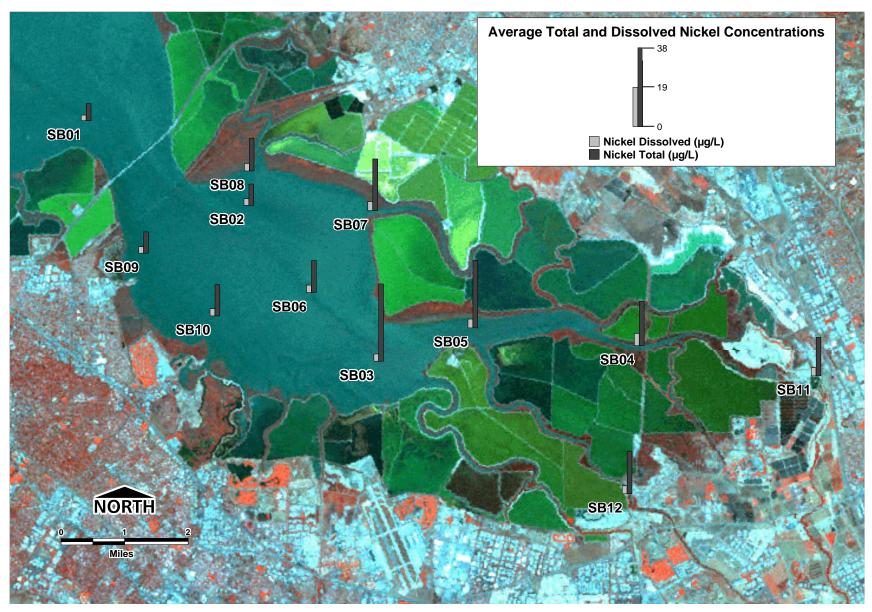
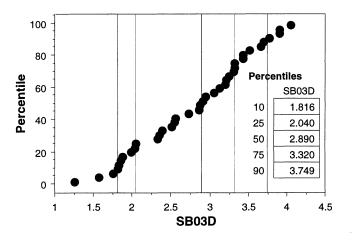
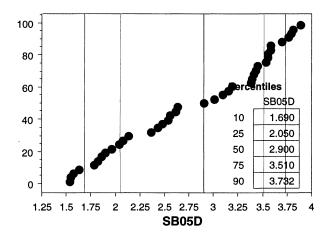
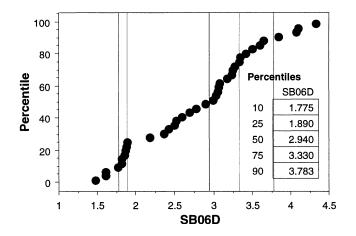


Figure 3-4. Average Total and Dissolved Nickel Concentrations Reported in City of San Jose South Bay Monitoring Program.







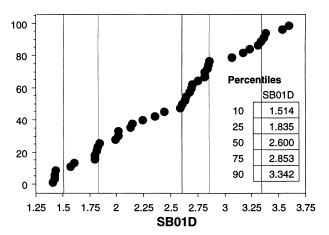


Figure 3-5. Cumulative distribution plots for dissolved copper concentrations measured at selected South Bay stations.

Dissolved copper concentrations at City of San Jose Stations SB01, SB02, and SB03 compared with RMP Stations BA30,BA20, BA10, and earlier data at SBDA Stations (left axis). The streamflow on the Guadalupe River is shown for the same period of time (right axis).

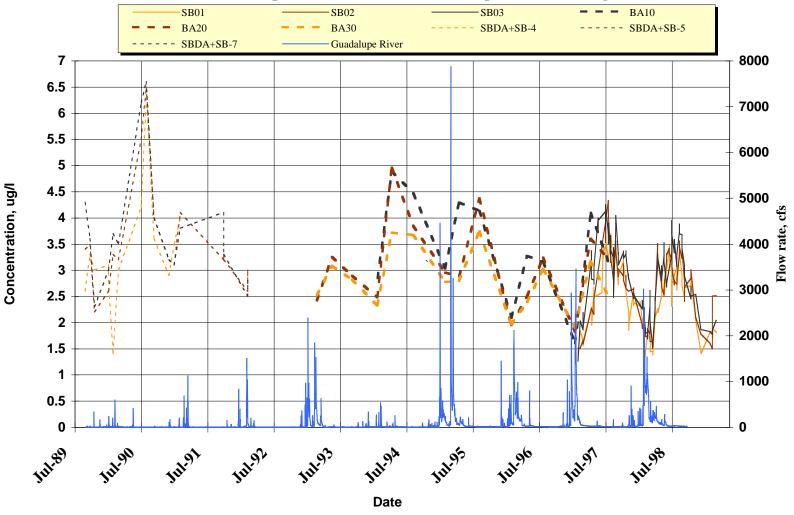


Figure 3-6. Time series for dissolved Cu in South Bay and flow on the Guadalupe River.

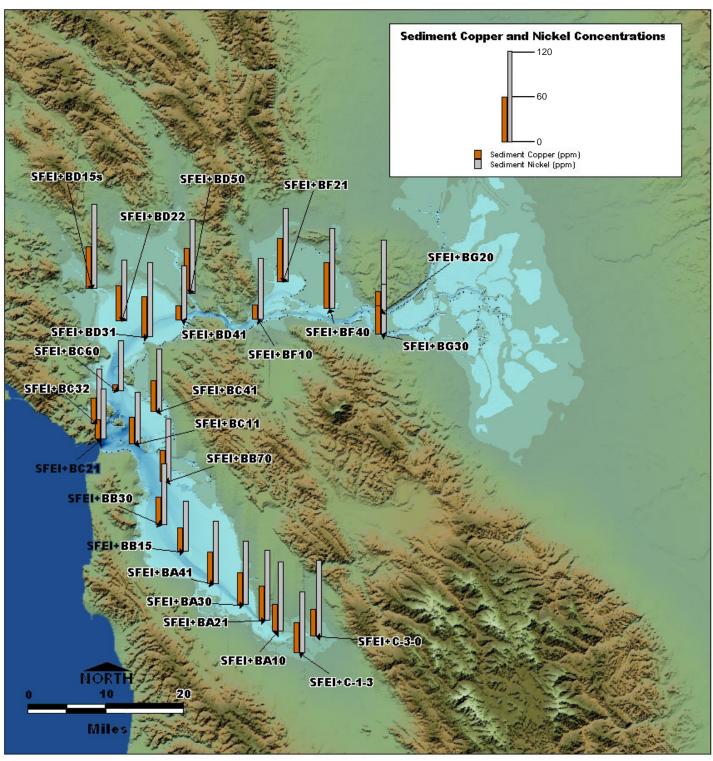
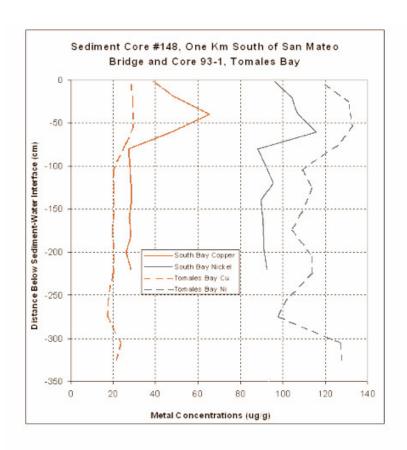


Figure 3-7. Surficial sediment copper and nickel concentrations at locations throughout San Francisco Bay.



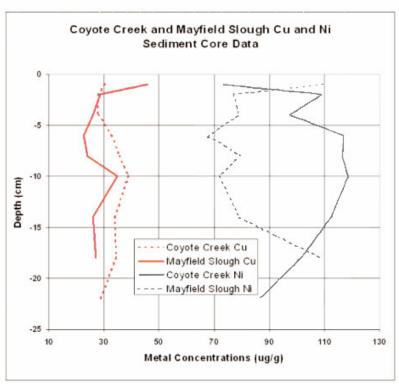


Figure 3-8. Copper and nickel concentrations in sediments taken from South Bay, Lower South Bay, and Tomales Bay (background).

# 4.0 DEVELOPMENT OF SELECTED INDICATORS FOR LOWER SOUTH SAN FRANCISCO BAY

Development of an indicator requires using site-specific information from within the Lower South San Francisco Bay, setting an indicator value, and applying that value to assess whether or not the beneficial uses of Lower South San Francisco Bay are being impaired. The purpose of this Section is to define the measurable quantities, the range of values for those quantities, and describe how the selected environmental indicators will be used to assess impairment in Lower South San Francisco Bay.

Seven indicators were originally considered for inclusion in the impairment assessment. However, when compared to the 11 Indicator Evaluation Criteria (Table 2-1), four of the indicators were found to be lacking in either data or applicability to the Lower South San Francisco Bay system (i.e., SEM/AVS, Benthic Macroinvertebrate Communities, Charismatic Macrofauna, and Phytoplankton). The indicators that were selected for the impairment assessment (Individual Species Toxicity Tests, Aquatic Ecological Risk Assessment Protocol (AERAP), and Site-Specific Studies) were indicators that either had adequate data or are currently being used to assess impairment to Lower South San Francisco Bay. The phytoplankton, while being inherently important to all of the Beneficial Uses of Lower South San Francisco Bay, had too many uncertainties associated with it to be used as a primary indicator of impairment and could be used only in a qualitative manner.

These indicators were not selected to be used alone, but rather as a suite of indicators; each one adding to the next. The Individual Species Toxicity Test Indicator is used to estimate the sensitivities of test species that are either resident or commonly used as surrogates for Lower San Francisco Bay to copper and nickel. The results of this indicator are used by the Aquatic Ecological Risk Assessment Protocol (AERAP) Indicator to estimate the local community response at the n<sup>th</sup> percentile. The AERAP Indicator uses regression analysis to provide a range of copper concentrations that are based on a desired level of protection (nickel was not used due to a lack of data). Each of these AERAP concentrations is then multiplied by a site-specific correction factor that is estimated by the Site-Specific Studies Indicator to provide a range of technically sound site-specific water quality objectives. These site-specific water quality objectives are then compared against the sensitivity results published in the phytoplankton literature and a site-specific water quality objective that is protective of the phytoplankton community is chosen.

In light of this, these indicators are presented sequentially by increasing levels of complexity. While each indicator does present an "indicator value", these individual values are not meant to be used, or interpreted as any final recommendation for a site-specific water quality objective; but the intent is to use them together in a final synthesis which will be presented in Section 5.

The following sections describe the development of each of the selected indicators.

# 4.1 Individual Species Toxicity Tests

The biological responses that are obtained from individual species toxicity tests are used to derive the maximum concentration of a chemical (e.g., copper and nickel) that is protective of the beneficial uses of a water body and the areas that the water body influences (e.g., marshes and sloughs). This concentration is called the "water quality criterion" and is currently being used as an indicator value to assess the potential of copper and nickel to cause impairment to beneficial uses of Lower South San Francisco Bay. This indicator is widely used and accepted by the regulatory, environmental, and regulated communities and provides the basis for the existing "water quality standards" (e.g., National Water Quality Criteria, National Toxics Rule (NTR), and the proposed California Toxics Rule (CTR)). The proposed national water quality criteria and local water quality objectives for copper are  $3.1~\mu g/L$  as dissolved copper and  $4.9~\mu g/L$  as total copper, respectively. The national water quality criterion and local water quality objective for nickel is  $8.3~\mu g/L$  as total nickel.

These criteria are based on aquatic toxicity bioassays that are performed in laboratory water (containing little or no apparent complexing capacity that could conceivably reduce copper and nickel toxicity) and provide "worst-case" estimates of impairment. As such, they do not take into account any characteristics of local water quality that may reduce or enhance the toxicity of these chemicals. In recognition of this, the U.S. EPA guidelines (Carlson, et al. 1984; NTR; and CTR) allow for modifications to these criteria based on 1) local water chemistry; 2) resident species sensitivities to copper and nickel; and 3) the new criteria must be protective of sensitive, commercial, recreational, and ecologically important species.

The San Francisco Bay Regional Water Quality Control Board (SFRWQCB) used this modification allowance in 1992 (S.R. Hansen & Associates, 1992 a, b) and recommended a water quality objective for copper in San Francisco Bay to be 4.9  $\mu$ g/L as total copper (this value was based on the national water quality copper criterion (2.9  $\mu$ g/L as total copper) in use at that time and the sensitivity of the oyster, *Crassostrea gigas* to copper in ambient, San Francisco Bay waters. This water quality objective was remanded in 1994 but is being used by the SFRWQCB for setting effluent limitations that are based on the best professional judgement determination, based on currently available information, that it is the best available water quality objective. The U.S. EPA has since proposed that the national water quality criterion be changed to a dissolved copper concentration of 3.1  $\mu$ g/L.

This section will address the history of water quality criteria, their application to Lower South San Francisco Bay, and how the appropriate application of this indicator can be used to assess impairment of the beneficial uses of Lower South San Francisco Bay.

# 4.1.1 Water Quality Criteria, an Historical Perspective

**Federal and State Regulatory Authority -** The Clean Water Act (CWA) (PL 92-500), originally enacted in 1972, requires the U.S. EPA to set water quality criteria for freshwater and saltwater to protect diverse aquatic organisms. These criteria are based on laboratory toxicity tests relating mortality to metals concentrations for a range of sensitive aquatic organisms.

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The law that governs the water quality regulations in California is the Porter-Cologne Water Quality Control Act (Division 7 of the California Water Code). This act details procedures which the State and the Regional Water Quality Control Boards must follow in water quality control planning, adoption of water quality objectives (comparable to federal standards), the issuance of waste discharge requirements, and enforcement. The policy of the Porter-Cologne Act is that the quality of all waters of the state shall be protected and factors affecting the water quality be regulated to attain the highest quality which is reasonable.

Water Quality Criteria Development - Environmental scientists have recommended using laboratory toxicity tests to estimate the concentrations of chemical pollutants that are protective of aquatic life for over 40 years. Water quality criteria concentrations for metals and other chemicals have been published since the 1950s (McKee and Wolf, 1952, 1963; Federal Water Pollution Control Administration, 1968 (Green Book); National Academy of Science/National Academy of Engineering, 1973 (Blue Book); U.S. EPA, 1976 (Red Book). Each of these had different methodologies and data requirements. It wasn't until the mid 1980's that criteria concentrations were set by the U.S. Environmental Protection Agency (U.S. EPA) using standardized procedures (Stephan et al. 1985). During this time period, the U.S. EPA first set standards for metal discharges into public waters by industry and municipal wastewater treatment plants. The regulations were based on toxicity test results in which aquatic organisms were exposed to metals in the laboratory. The concentration that were used in these lab tests were reported as total metal concentrations, and this approach was adopted in the standards.

Numerical water quality criteria derived using EPA's 1985 guidelines are expressed in terms of both a short-term and a long-term value, rather than a single value, in order that the criteria more accurately reflect toxicological and practical realities. This criterion is composed of two parts 1) Criteria Maximum Concentration limit (CMC), a short-term concentration acute exposure limit and 2) a Criteria Continuous Concentration (CCC), a four-day average concentration chronic\* limit. This allows for the protection of the beneficial uses based on both acute (short-term) and chronic (long-term) exposure of a toxicant to sensitive aquatic organisms without being as restrictive as a single-value criterion would be (U.S. EPA 1997). A two-part criterion is used because organisms can tolerate higher pollutant or chemical concentrations, as represented by the CMC, provided that the magnitude of the concentration and the duration and frequency of the exposure period are limited (Hansen 1989). Aquatic organisms do not generally experience steady pollutant exposure, but rather fluctuating exposures over time and can generally tolerate higher concentrations of pollutants if the exposure period is short. In light of this, the U.S. EPA makes allowances for a pollutant to exceed the CCC if 1) the magnitude and duration of exceedences are appropriately limited and 2) there are compensating times when the concentration is below the CCC. The acute criterion (CMC) cannot be exceeded more than one hour in three years on the average and the chronic criterion (CCC) for a pollutant not be exceeded more four days every three years on the average.

The U.S. EPA Guidelines (Stephan et al 1985) derive the saltwater copper and nickel CMC values from data based on the acute toxicity of those metals to saltwater aquatic life using a minimum number of tests and specific families of organisms. This methodology:

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- Ranks the order of the acute sensitivity of different aquatic genera (sensitivity within
  a genera are averaged to produce a Genus Mean Acute Value (GMAV) and ranked
  from least sensitive to most sensitive genus);
- Uses the acute values for the four most sensitive genera; and
- Uses the total number of genera to calculate the Final Acute Value (FAV) using modified regression analysis.

The FAV represents that concentration above which 95% of the average acute values (LC50s or EC50s) for genera occur. The CMC is derived by dividing the FAV by 2 (a factor that is the average ratio of LC50s to LC0s). If there is a species of commercial, recreational, or ecological value that is not protected by using a FAV generated by using the GMAV then the Species Mean Acute Value (SMAV) (the mean of acute sensitivity values for that species) of that more sensitive organism is substituted for the GMAV.

## 4.1.2 National and San Francisco Bay Water Quality Criteria History

In 1985, the U.S EPA set the FAV for copper at  $5.8 \,\mu g/L$  and the CMC at  $2.9 \,\mu g/L$  (total recoverable). The National Criteria are usually used without consideration of site-specific water quality. There are, however, provisions which allow for regulations to be set which take into consideration site-specific effects of water quality on metals' bioavailability. This procedure, called a Water Effect Ratio (WER), involves determining the ratio of metal toxicity in side-by-side bioassay tests using ambient site and laboratory waters. Applying a WER to the national criterion is one way to derive effluent limits that are fully protective of beneficial uses, while not being overly protective.

Several studies conducted on San Francisco Bay waters indicated that the Bay did indeed have considerable metal complexing capacity with WER values ranging from 1.2 to >10 for copper and from 0.9 to 17 for nickel (Larry Walker Associates et al. 1991a, b; S.R. Hansen & Associates 1992a, b). Using these studies, the San Francisco Regional Water Quality Control Board (SFRWQCB) proposed a copper water-effect ratio (WER) of 1.7 (based on total copper) for the entire San Francisco Bay. The SFRWQCB adopted this WER when it amended the Basin Plan (1995) to replace the copper objective of 2.9  $\mu$ g/L with 4.9  $\mu$ g/L (total recoverable copper) (2.9  $\mu$ g/L X 1.7 = 4.9  $\mu$ g/L) (described in detail in Section 4-3).

The U.S. EPA (1984) acknowledged that, because of bioavailability effects, water quality criteria (with respect to metals) were likely to be too conservative for many natural waters. In 1993, the U.S. EPA (Prothro, 1993) issued interim guidance allowing dissolved metal concentration instead of total metal concentration to be used to set and measure compliance with the water quality criteria. In 1995 the U.S. EPA proposed a change to the saltwater national copper criteria to reflect new data and to change the criteria from total recoverable to dissolved concentrations. Unmeasured, unconfirmed metals' data for the blue mussel, *Mytilus edulis* were replaced by three ToxScan (1991a, b, c: Larry Walker Associates et al. 1991a, b) and four Science Applications International Corporation (SAIC 1993) measured and confirmed metals values. The resultant FAV was higher than the Species Mean Acute Value (SMAV) for *M*.

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edulis<sup>1</sup> and so the FAV was lowered from 10.39 to 9.625  $\mu$ g/L copper to protect the commercially important *M. edulis* (U.S. EPA 1995). Thus, *M. edulis* determines the proposed saltwater criterion for copper and the resultant national saltwater criteria were raised from 2.9  $\mu$ g/L (total) to 3.1  $\mu$ g/L (dissolved) (Draft CTR, 1997).

The U.S. EPA (1986) calculated the FAV for nickel to be 149.2  $\mu$ g/L, the CMC to be 74.60  $\mu$ g/L, and the CCC to be 8.293  $\mu$ g/L as total nickel. The CCC value represents the nickel Water Quality Standard established for San Francisco Bay through implementation of the Basin Plan.

It is derived from dividing the FAV by the Final Acute-Chronic-Ratio (FACR) of 17.99 (equation 1). The FACR is derived by taking the geometric mean of all freshwater and saltwater Acute-to-Chronic Ratios in the data-set and is used to convert acute toxicity data to a chronic value upon which a CCC can be set. The water quality objective for nickel in San Francisco Bay is 8.3 µg/L (as total nickel).

Watson, et al (1996, 1999) updated the national data-set by deleting non-native species, eliminating questionable data from the data set, adding additional saltwater acute and chronic test data to the data-set, and recalculating a new "proposed" national and site-specific criterion for nickel. The recalculated national and South San Francisco Bay site-specific FAVs were 145.5  $\mu$ g/L and 124.8  $\mu$ g/L, respectively, with the FACR being either 10.50 (using a combination of freshwater and saltwater ACRs) or 5.959 (Using only the four marine species ACRs). Using these values, Watson, et al (1996, 1999) was able to justify that a new national and site-specific criterion for nickel be set at 13.86 and 11.89  $\mu$ g/L, respectively (equations 2 and 3) using the combined ACR. And a new national and site-specific criterion for nickel was calculated to be 24.42 and 20.94  $\mu$ g/L, respectively (equations 4 and 5) when the marine ACR is used.

Formula:	$FAV \div ACR = CCC$
Equation 1	$149.2 \ \mu g/L \div 17.99 = 8.293 \ \mu g/L$
Equation 2	$145.5 \ \mu g/L \div 10.50 = 13.86 \ \mu g/L$
Equation 3	$124.8 \ \mu g/L \div 10.50 = 11.89 \ \mu g/L$
Equation 4	$145.5 \ \mu g/L \div 5.959 = 24.42 \ \mu g/L$
Equation 5	$124.8  \mu \text{g/L} \div 5.959 = 20.94  \mu \text{g/L}$

Regardless of which ACR is used, this study indicates that the current national nickel water quality criterion and San Francisco Bay water quality objective (8.3  $\mu$ g/L as total) is most likely overprotective of the beneficial uses of Lower South San Francisco Bay.

<sup>&</sup>lt;sup>1</sup> The lowest value must be selected when needed to protect local commercially or recreationally important organisms.

## 4.1.3 Quality of Available Data

The toxicity bioassay data that have been used to calculate water quality criteria for copper and nickel undergo extensive quality control/quality assurance protocols. This begins with the initiation of the individual toxicity bioassay tests. These tests are performed under rigorous quality control criteria as described in the appropriate EPA testing protocols. The final data values are then subjected to a rigorous peer review, where they are compared to the minimum quality control criteria that are required for usage in calculating the national water quality criteria (Stephan et al. 1985). If the data meet the minimum acceptance requirements, they are used to calculate a criterion; if they are found to be deficient, they are rejected.

The data set representing the acute sensitivity of marine and estuarine organisms to copper is much more complete than is the data set representing nickel. There is, however, a paucity of data regarding the chronic effects of copper and nickel on marine and estuarine organisms. This lack of chronic sensitivity data results in criteria that use both fresh and saltwater sensitivity data to derive a saltwater criterion. For example, the nickel criterion (EPA 1986) uses the geometric mean from one marine organism (*Mysidopsis bahia* ACR = 5.48) and two freshwater organisms (*Daphnia magna* (ACR = 29.86) and *Pimephales promelas* (ACR = 35.58)) to derive the saltwater FAV. The resultant FACR of 17.99 is more than 3 times greater than the ACR for the local marine organisms and, in fact, most likely provides criteria that are over-protective of beneficial uses.

## 4.1.4 Can this Indicator be used in Lower South San Francisco Bay?

The U.S. EPA (through the CTR) is proposing that water quality criteria derived through using this indicator be used to fill a gap in the State of California water quality standards. This gap was created in 1994 when a State Court overturned California's water quality control plans which contained water quality criteria for priority toxic pollutants for which the EPA had issued CWA water quality criteria guidance (Section 304 (a) CWA) (U.S. EPA, 1997). As a result, this indicator could not only be used for Lower South San Francisco Bay, but for all of the State of California. The SFRWQCB currently uses water quality criteria that are based on this indicator and WER studies for guidance in setting discharge permit limits in San Francisco Bay. In reissuing these discharge permits, the SFRWQCB relies on the available scientific data to identify a range of final water quality objectives for copper and nickel.

Selecting Resident and Surrogate Species - While water quality criteria developed by this indicator are currently being considered as part of the state-wide CTR, many of the test species data that are included in the present database are not necessarily residents of Lower South San Francisco Bay. (Appendix D) presents a comprehensive listing of toxicity test results from 137 copper toxicity tests on 46 different species and 49 nickel toxicity tests on 27 different species and covers a time span of 40 years. This table includes the test results that were used in setting the national saltwater water quality criterion for copper (1996) and nickel (1986), as well as the results of other tests that were located in the literature. In addition, this data set is divided into species and genera which are resident to Lower South San Francisco Bay, those that are commonly used as surrogate test species for Lower South San Francisco Bay, those species that

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meet the guidelines described in the "WER Cookbook" (U.S. EPA, 1994) for species deletions, and those species which are non-natives to Lower South San Francisco Bay. The breakdown, based on 73 species tested for copper and nickel, is as follows:

- Resident species and/or genera = 40% of the total,
- Commonly used surrogate species = 15% of the total, and
- Non-native species = 45% of the total.

Of the species or genera that are native to Lower South San Francisco Bay, 86% have reported sensitivities to copper that lies between 5 and 10 µg/L. None of the resident species that are listed in the nickel data set are among the "most sensitive" organisms to nickel. One resident genus (the diatom, *Thalassiosira*) and one commonly used surrogate species (red abalone, *Haliotes rufescens*) exhibit chronic responses to nickel at concentrations as low as 44.5 and 48.3 µg/L, respectively. It should be noted however, that many of the test results reported in Appendix C were performed in "clean" laboratory or culture water that contains little or no metal complexing capacity. Thus the results reported can be assumed to be "worst-case".

The toxicity results of these resident and surrogate species are used to recalculate a site-specific water quality standard that is more representative of local beneficial uses. This calculation is performed as part of the AERAP Indicator (Section 4.2) which provides a range of concentrations that can be used to set a site-specific water quality objective.

Water Quality Attainment - Water quality criteria developed by using the sensitivities of aquatic species to copper and nickel are currently being applied either directly (nickel) or indirectly (copper via WER correction) in San Francisco Bay by comparing them to the ambient concentrations of copper and nickel (Section 2.0). Ambient concentrations above the criteria are assumed to pose potential threats to beneficial uses.

Copper - Comparisons of ambient Lower South San Francisco Bay dissolved copper concentrations to the current National and proposed CTR water quality criterion for dissolved copper of 3.1 µg/L are summarized in Figure 4-1. This figure is a graphical representation of the data collected between 1989 and 1999 by the San Francisco Bay Regional Monitoring Program (RMP); the Lower South San Francisco Bay WER study (City of San Jose, 1998); and the South Bay POTW Monitoring Program. These data indicate that approximately 52 percent (128 out of 245 samples) of the ambient dissolved copper concentrations measured during the above mentioned time period were above the National and proposed CTR saltwater water quality criterion.

**Nickel** – Comparisons of ambient Lower South San Francisco Bay dissolved nickel concentrations to the National water quality criterion and local water quality objective, and proposed site-specific water quality objectives for nickel (Watson, et al. 1996, 1999) are summarized in Figure 4-2. This figure is a graphical representation of data collected between 1989 and 1999 by the San Francisco Bay Regional Monitoring Program (RMP); the Lower South San Francisco Bay WER study (City of San Jose, 1998); and the South Bay POTW Monitoring

Program. The data are compared to the above mentioned criterion, objective, and proposed criteria. The ambient Lower South San Francisco Bay dissolved nickel concentrations were sporadically above the National saltwater criterion and the San Francisco Bay water quality objective of 8.3  $\mu$ g/L (13 out of 245 samples, or 5 percent) during this ten year period. Ambient dissolved nickel concentrations were greater than the proposed SSO of 11.89  $\mu$ g/L (combined freshwater and marine ACRs) once during this same time period (1 out of 245 samples, or 0.4 percent).

#### 4.1.5 Uncertainties and Issues

The consequences of the decisions that are made regarding the setting of site-specific objectives extend well into the future. For this reason, it is essential that predictions of the effects of allowable concentrations of copper and nickel in Lower South San Francisco Bay be technically sound and based on the best available scientific information. However, the presence of uncertainty complicates the ability to make absolute statements and thus, technically based estimates can only be made. In addition, decision-makers need to be provided a measure of the magnitude of the uncertainty associated with decision criteria to then be able to effectively weigh and use the results of these environmental analyses. These issues are addressed in the impairment assessment by making a vigorous effort to identify the magnitude and sources of uncertainty associated with each of the indicators that are used in the impairment assessment and that are used in the development of alternatives for site-specific objectives.

Uncertainty is defined herein as the state or condition of incomplete or unreliable knowledge. For each indicator evaluated or analysis conducted in this assessment, both the sources and the magnitude of known uncertainties are identified. The sources include natural variability, sample variability, and the appropriateness of models that are used in making predictions. Where possible, the magnitudes of identified uncertainties are addressed using descriptive statistics and by setting confidence limits on predicted values. In the absence of quantitative information, a professional judgement of the value of the existing information is presented.

The uncertainties and issues that are associated with this indicator are listed below:

**Uncertainty -** The assumption that the response of a test organism to a given stressor (when exposed at a sensitive life stage) mirrors the response that the test organism would exhibit if exposed to the stressor for its entire life provides some uncertainty. Ideally, aquatic toxicity bioassay tests would expose the test organism to a stressor for the duration of its life-cycle (cradle-to-grave). In actuality, only the easiest "most sensitive life stage" (generally, an early life stage) is what gets tested (due to the logistics and cost of full life-cycle tests). The exposure may be either short-term (acute - from a few minutes to 4-days) or longer-term (chronic - one week to 90 days.

**Resolving this Uncertainty -** The early life-stage of most organisms is when they're most sensitive to toxicants (e.g., copper and nickel). For this reason, the use of early life-stages is a general requirement of most toxicity testing protocols (U.S. EPA 1991). Therefore, if the exposure to a toxicant occurs during the early life-stage (i.e., the most sensitive life-stage) the resultant toxicological value (and subsequent water quality

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criterion) would be protective of that organism and, as such, partial life-cycle tests which use early life-stage organisms provide an adequate measure of protection. In addition, this report used the most conservative Acute-to-Chronic Ratio (ACRs) which ultimately reduces uncertainty regarding short-term vs. long-term exposure.

**Recommended Action -** None. All tests used early life-stage organisms.

**Uncertainty** - Direct projection of toxicity test results obtained under very controlled laboratory conditions to predict ambient toxicity responses limit the accuracy and add uncertainty to any analysis. Several conditions (e.g., toxicant exposure, temperature, photoperiod (light intensity and duration), and presence or absence of predatory stress) have the potential to be much different between the laboratory and ambient site (Diamond et al. 1999 et al. and citations therein).

Resolving this Uncertainty - This uncertainty can be reduced by adequately characterizing the ambient conditions prior to testing. Many of the ambient conditions can be duplicated, to some extent, in the laboratory (e.g., photo-period and intensity can be duplicated by using appropriate lighting and timers/dimmers; ambient temperature can be duplicated by using thermo-controllers; and salinity can be maintained using natural or artificial salts). These will only serve to reduce the uncertainties since the effects of environmental fluctuations (e.g., cloud cover, freshwater runoff/rain, and predators) cannot be easily duplicated.

**Recommended Action -** None. All toxicity tests used standardized bioassay protocols which include controlling environmental factors to the greatest extent possible.

**Uncertainty** - These tests were performed in laboratory water which has, by definition, little or no apparent complexing capacity which could mediate copper and nickel toxicity. This means that the test results are "worst-case", in that it is assumed that the test organism is being exposed and responding to "All" of the copper or nickel in the test solution. Test organisms do however, produce organic substances (e.g., waste products) that can affect the complexing capacity of test water. Since complexing capacity is not a water quality parameter that is generally tested, there is no available information regarding whether complexing capacity changed during the testing period. Uncertainty is added when criteria are derived using these "worst-case" results and applying them to ambient conditions. Under ambient conditions, there are several compounds (organic chelators) and inorganic ions which either bind to the copper or nickel (making them biologically inert) or compete for binding sites on the organism. In addition, The effects of multiple stressors (e.g., synergism, antagonism, or additivism) on a test organism are not addressed by laboratory toxicity bioassay tests. These effects can either exacerbate the response to a given toxicant (synergism), reduce it (antagonism), or directly add to it (additivity).

**Resolving this Uncertainty -** Using this indicator and the resulting water quality criteria in conjunction with ambient site-specific tests would eliminate, or reduce the uncertainties associated with comparing test results that were obtained from laboratory

water to test results obtained using ambient water. Laboratory water tests are relatively "simple" solutions using only a single toxicant and water containing little or no binding capacity. Whereas, ambient waters tend to be "complex" solutions (e.g., *in situ* conditions would have potentially multiple toxicants or stressors and binding capacity). It would also take into consideration the effects of additivity, antagonism, and synergism on copper and nickel toxicity.

**Recommended Action -** Use only in conjunction with a site-specific multiplier (e.g., WER or ACR).

**Uncertainty -** The uncertainty based on the assumption that using surrogate test species provides an adequate estimate of the sensitivity of native species to a particular toxicant depends on the quality of the surrogate test organisms. Laboratory culturing of these surrogates imparts uncertainty to tests regardless of whether the species is fundamentally appropriate to use as surrogates. Nutritional and behavioral requirements of these surrogate species are not fully understood, which may lead to variable results in toxicity testing that have no actual relationship to indigenous biota. Many of the species that are used in these toxicity tests are non-resident and, therefore, surrogate test species (closest genus match) are used.

**Resolving this Uncertainty -** There is a certain amount of controversy regarding the appropriateness of using test surrogates. Stephan et al. (1985) states that, "On the average, species within a genus are toxicologically much more similar than species in different genera." He also states that applying the appropriate surrogate will provide an adequate amount of protection for resident species. The level of uncertainty associated with surrogates can be reduced by adequately characterizing the culturing requirements of a proposed surrogate test species prior to its use. In addition, it is imperative that careful attention be paid to the health of the culture stock health.

**Recommended Action -** Generate a "resident species" data-set. In the interim, use only surrogate species that appropriately represent the resident species population. This means using surrogates that are as closely related to residents as possible (i.e., same genera) and were obtained from reputable culturing facilities.

Uncertainty - There is a level of uncertainty associated with the organisms that comprise the national data-set. This uncertainty arises with the possibility that there are resident organisms that are more sensitive to copper and nickel than those in the data-set that either cannot or have not been tested due to difficulties in collection, culturing, and testing. The paucity of data on phytoplankton assemblages (cyanobacteria, coccolithophores and dinoflagellates) that have been reported to be more sensitive to copper than the species that are included in the national database could, if quality information is not available, cause these organisms to be non-protected. The existence of species that are more sensitive to copper than those included in the national data-set present a level of uncertainty as to whether there are other species (perhaps more ecologically relevant) which are more sensitive to copper and are not being protected.

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**Resolving this Uncertainty -** Plants and algae species are not generally used to set water quality criteria because of the difficulty in interpreting the results. This is because the sample must be filtered and have nutrients added prior to commencing the test. These procedures can potentially alter the bioavailability of metals and adds uncertainty about what the organisms are being exposed to. However, plants and algae should be protected (if they are ecologically important) (Mount 1992). The lack of adequate toxicological data on these sensitive phytoplankton assemblages could be remedied by performing standardized toxicity tests using them. This would add to the national data-set and, if necessary, allow for the re-calculation of a criterion that would be protective of them. On the whole, the U.S. EPA (1984) states that a criterion that is protective of the most sensitive aquatic animal should also be protective of phytoplankton. Identification of sensitive resident species and determination of the toxicology of copper and nickel would be the first steps in addressing the potential for ecologically important species that currently remain unknown and, possibly unprotected. In addition, the project chose to use several resident plant genus/species toxicity measures to more fully assess the risk to community assemblages.

**Recommended Action -** Fully characterize the components of the ambient water. Knowledge of what comprises any observed apparent complexing capacity will allow for a more complete understanding of how metals bioavailability can be influenced by filtration and added nutrients. In addition, resident phytoplankton species need to be isolated and their sensitivities to copper and nickel determined in both laboratory and ambient waters.

#### 4.1.6 Conclusions

The results that are obtained from using this indicator are currently being used on the federal, state and, with some modifications, the local level. This indicator is not appropriate, however, to be used directly to set water quality criteria for Lower South San Francisco Bay since:

- several studies have demonstrated that ambient San Francisco Bay and Lower South San Francisco Bay waters have the ability to significantly reduce copper toxicity when compared to test results obtained from clean laboratory water and
- nickel criterion recalculation studies using resident and native west coast test organisms have indicated that the current national and local water quality criteria/objectives are over-protective by as much as 1.5 to 2.6 times when compared to the site-specific recalculated criteria as described by Watson, et al. (1996, 1999).

The most appropriate use of this indicator would be to include the species' sensitivity results in the AERAP Indicator analyses which uses regression analysis to provide a water column copper concentration which is "community based". This value would then be modified by a Lower South San Francisco Bay water quality characteristic multiplier "WER" to provide a final site-specific water quality criterion/objective that would be fully protective of the beneficial uses of Lower South San Francisco Bay without being over-protective.

## 4.2 Aquatic Ecological Risk Assessment Protocol (AERAP)

The Aquatic Ecological Risk Assessment Protocol (AERAP) was developed by the Water Environment Research Foundation to provide a community-level interpretation of individual species laboratory toxicity tests. The AERAP indicator predicts effects as a percent of taxa in the community that are potentially impacted by ambient concentrations of a pollutant. The values produced by the protocol are only indicators of community response since the protocol does not attempt to simulate the effect of other stressors that may be present or any changes in interactions between community components (e.g., the effect of reduced prey species on community structure). The protocol can evaluate the effects of more than one pollutant, but the analysis is additive and does not capture any potentially synergistic effects. The protocol provides a simple description of community response to toxicity, rather than evaluating species response on an individual basis.

### 4.2.1 Description of the Indicator

The AERAP can be applied to chemicals in surface water and sediments to estimate their ecological effects at the community level. This indicator allows stakeholders to combine the results of individual toxicity tests and evaluate potential impacts under various exposure scenarios. The exposure scenarios can be based on measurements of existing concentrations (*Expected Environmental Concentrations* – EEC) or estimated concentrations. The model can also be used to estimate the *Ecological Risk Criterion* (ERC) that is protective of a specified percentage of community taxa for the pollutant being evaluated. The Ecological Risk Criterion is the water quality concentration of a pollutant that has been calculated for protection of community taxa at a specified level (e.g., 95%). The protocol can also be used to test risk hypotheses related to community level impacts due to exposures to copper. The AERAP combines the information on the toxicity of copper to resident species of San Francisco Bay with measurements of ambient water quality concentrations to generate probabilistic measures of impact.

The AERAP was not used as an assessment tool for nickel because its addition would not have added any additional value to the results obtained by the City of San Jose during their "Recalculation of the National Marine Water Quality Criterion and Development of a Site-Specific Nickel Criterion" study. This study used the procedures described in the WER Cookbook to update the National data set and recalculate a new national water quality criterion for nickel that was based on site-specific species composition. Since this procedure had already been used by the City to calculate several potential site-specific water quality objectives for the South Bay, it will not be necessary to use the AERAP to accomplish a very similar objective.

The AERAP Tier 3 assessment includes quantitative, probabilistic, and more ecologically relevant estimates of risks than a simple comparison of an individual species test to a water quality criterion. For example, the AERAP provides the capability to estimate the percent of fish and invertebrate taxa affected by acute or chronic toxicity. It also includes quantitative assessments of uncertainties in risk estimates attributable to data quality, variability, or assumptions used in the analysis. The toxicity database that is included with the AERAP is the

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EPA freshwater criterion database, which includes few marine organisms or species resident to South San Francisco Bay. The project team compiled toxicity databases that include organisms more appropriate for an analysis of conditions in South San Francisco Bay. These databases are described in Section 4.1. The project team used the quality assurance guidelines required by U.S. EPA for their criterion database in selecting toxicity tests to include. Using a resident species database reduces unacceptably large uncertainties on estimates of risk for pollutants of concern.

The AERAP analysis provides the capability to conduct an assessment that goes beyond a simple comparison to EPA's acute and chronic ambient water quality criteria. The AERAP ecological effects characterizations are based on evaluating the full range of sensitivity of aquatic species to each chemical of concern. The AERAP risk characterization methods provide distributions of risk estimates, which are derived from integration of the entire environmental distribution for concentrations of each chemical with the entire distribution of toxicity data for each chemical. The data for these distributions come from single species aquatic toxicity tests. With these types of data, logistic regression models are developed relating the distribution of chemical concentrations to the probability of predicted community-level effects.

The output of the logistic regression model applied to the EPA acute freshwater copper toxicity database is illustrated in Figure 4-3. The x-axis is the range of copper concentrations from individual species toxicity tests. The y-axis is the cumulative frequency curve for interpolating the percent of taxa affected at any chosen copper concentration. To estimate the potential impact of an estimated or measured concentration of dissolved copper draw a line perpendicular to the x-axis from the selected concentration until it intersects with the cumulative frequency curve. Next draw a line to the y-axis to identify the cumulative percentage of species affected.

The models can be generic to all species in the United States or specific to the species inhabiting a region or site. The assumptions included in the models are the following:

- As the concentration of chemical of potential concern (COPC) increases, the number of species in the community affected by acute and chronic toxicity increases.
- The relationships between concentrations of COPC and effects on the community of aquatic species can be estimated from data on single species toxicity tests.
- The relationships represent those found in natural aquatic communities exposed to these COPC.
- There are no confounding effects of habitat, water quality, flows, bioavailability, or species (such as competition and predation).
- A description of the statistical procedures and associated assumptions are included in Appendix E.

The WERF aquatic ecological risk assessment methods are unique because they provide quantitative and probabilistic risk estimates. Many existing risk assessment methods provide only qualitative deterministic risk estimates and answers the question "is there a risk?" These

methods do not evaluate the uncertainty in the estimates of exposure and toxicity used in the assessment. This can lead to the impression that the results of a simple risk assessment are very precise, when in fact they are imprecise and uncertain. The AERAP evaluates these uncertainties and answer the question "what is the risk?" For example, risk could be characterized as "less than a 5% (1 in 20) probability that the concentrations of copper in South San Francisco Bay will cause chronic toxicity to 5% or more of the aquatic species in the bay," or "virtually certain (>99% probability) than the concentrations of copper in South San Francisco Bay will cause chronic toxicity to 20% or more of the fish and benthic macroinvertebrate species in the Bay."

Benefits of the WERF aquatic ecological risk assessment methods include the following.

- The methods are applicable to single chemicals or combinations of multiple chemicals.
- The methods can be applied at different geographic levels to assess risks of toxic chemicals at single sites within water bodies, a portion of a water body, an entire water body, or an entire watershed.

The AERAP has been used successfully for other similar assessments at several locations in the United Sates. These applications of the AERAP have been conducted with peer review procedures in place. U.S. EPA includes the AERAP in its 1998 "Guidelines for Ecological Risk Assessment." Its selection for use in South San Francisco Bay is well founded in precedence.

#### 4.2.2 Available Information

The Tier 3 AERAP analysis requires toxicity information on resident species and water quality concentrations of the pollutant being evaluated. The toxicity database discussed in section 4.1.1 was the source of information copper and nickel toxicity on resident organisms in South San Francisco Bay. The project team conducted a literature search to identify copper toxicity testing information for species indigenous to South San Francisco Bay or close surrogates for resident species. The project team was able to identify an adequate amount of information for copper. Copper toxicity information for twenty-six resident and surrogate species and genera has been identified. These species included nine families, which exceeds the EPA guidelines (EPA 1994) for site specific objectives.

# Copper Toxicity Database

EPA's Guidelines for Ecological Risk Assessment (U.S. EPA 1998) lists some important considerations when comparing cumulative exposure and effects distributions for chemical stressors:

- Does the subset of species for which toxicity test data are available represent the range of species present in the environment?
- Are particularly sensitive (or insensitive) groups of organisms represented in the distribution?

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• If a criterion level is selected – e.g., protect 95 % of species – does the 5% of potentially affected species include organisms of ecological, commercial, or recreational significance?

The copper toxicity databases for the Lower South San Francisco Bay assessment are included in Appendix F. The Appendix table includes four different databases that were evaluated as part of the assessment including:

- 1. EPA National Copper Toxicity database for saltwater organisms
- 2. EPA National Copper Toxicity database for saltwater organisms amended using EPA Water Effects Ratio Cookbook guidelines
- 3. Lower South San Francisco Bay Resident and Surrogate Species
- 4. Lower South San Francisco Bay Resident Species.

The databases include a wide range of species found in the bay representing most ecological niches. The databases also include several of the most sensitive species found in the Bay. A summary of the AERAP species acute sensitivity database used in the analysis is included in Table 4-1. Appendix F identifies the subset of species used for each of the analyses. The most sensitive species included is the larval life stage of the blue mussel Mytilus edulis (LC50 9.63 $\mu$ g/L as dissolved Cu). The most resistant is a fish (*Rangia cuneata* LC50 = 6,925  $\mu$ g/L as dissolved Cu). The spread of species along the sensitivity gradient is evenly distributed, without large representation at one extreme or the other.

It was not possible to include plants in the AERAP analysis because the protocol uses acute toxicity values to generate the community response curves. Acute to chronic ratios (ACRs) were then applied to the ERCs that were generated by the protocol. Tests using single cell organisms are considered chronic and there is no need to apply an ACR, therefore plants were not used in the AERAP analysis. The community response values that were developed using organisms were compared to plant toxicity values to ensure that any recommended values would also be protective of plants.

Table 4-1
AERAP Species Acute Sensitivity Database

Species	LC <sub>50</sub> (ug/L) as Dissolved Cu
Mytilus edulis	9.63
Paralichthys dentatus	11.56
Mulinia lateralis	17.70
Crassostrea gigas	17.84
Arbacia punctulata	21.40
Crassostrea virginia	25.67
Acartia tonsa	27.65
Mya arenaria	35.10
Haliotes cracherodil	45.0
Acartia clausi	46.80
Homarus americanus	62.35
Haliotes rufescens	77.47
Pseudopleuronectes americanus	107.0
Phyllodoce maculata	108.0
Menidia beryllina	111.1
Menidia menidia	112.5
Mysidopsis bigelowi	117.0
Pseudodiaptomus coronatus	124.2
Menidia peninsulae	126.0
Neanthes arenaceodantata	150.6
Mysidopsis bahia	157.0
Nereis virens	206.7
Tigriopus californica	212.4
Atherinops affinis	218.7
Leistomus xanthurus	252.0
Cyprinodon variegatus	305.4
Nereis diversicolor	327.4
Trochinotus carolinas	370.5
Eurytemora affinis	473.4
Cancer maenas	540.0
Fundulus heteroclitus	1391.0
Rangia cuneata	6925.0

Values from the U.S. EPA Ambient Water Quality Criteria Document - Saltwater Addendum 1995.

The AERAP analysis used acute endpoints were used to calculate the ERC values for each of the four toxicity databases. Each acute ERC value was then converted to a chronic ERC value by dividing it by 3.127. The ACR value of 3.127 is the most conservative value (i.e., the highest) that could be used. For example, the Draft Final Copper Criteria Document, currently under review by the U.S. EPA, recommends a saltwater ACR of 2.388 (Gary Chapman, U.S. EPA personal communication with City of San Jose, 1/21/99).

While we recognize the importance of salmonid fish species in the Lower South San Francisco Bay, they were not included in the database that was used for the AERAP Indicator. This is because the available toxicity data were for freshwater exposures only and their inclusion in the database would inappropriately skew the final ERC. Several studies have indicated that toxicity

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of copper to juvenile salmonid fish is inversely proportional to water hardness (U.S. EPA 1984) which means that juvenile salmonids would be less sensitive to copper in a saline (increased hardness) system than in a strictly freshwater (decreased hardness) system.

The assumptions used in setting the criterion protection level will be discussed in the following section.

## Water Quality Database

The water quality data used in the AERAP analysis comes from four sources: 1) San Francisco Estuary Institute Regional Monitoring Program(RMP), 2) City of San Jose South Bay Monitoring Study, 3) South Bay Dischargers Association Monitoring Program, and 4) The City of San Jose WER Study. Water quality monitoring stations were selected using the following rationale:

- The distribution of stations should adequately characterize the range of natural conditions in South San Francisco Bay including open water, shallow water, and slough areas.
- Some portion of the stations should be located near known discharge points where concentrations of copper would be expected to be higher.
- Selected stations are those that are locations that are sampled by the City of San Jose
  Monitoring and WER studies, the South Bay Dischargers Association monitoring
  study, and the Regional Monitoring Program (RMP). This increases the number of
  samples that can be used to characterize anticipated exposures (Expected
  Environmental Concentrations EECs).

The stations selected are listed in Table 4-2 and illustrated on the map in Figure 4-4.

Table 4-2
Water Quality Monitoring Stations Used in the AERAP Analysis

	Station		
SBDA	San Jose (WER)	South Bay	RMP
(1989-1992)	(1996-1997)	(1997-1999)	(1993-1997)
	DBN	SB01	
SBDA+C-3-0	DBS	SB02	C-3-0
SBDA+C-5-0	CC	SB03	BA-10
SBDA+C-6-0		SB04	BA-20
SBDA+R-4		SB05	BA-30
SBDA+SB-4		SB06	
SBDA+SB-5		SB07	
SBDA+SB-6		SB08	
SBDA+SB-7		SB09	
		SB10	
		SB11	
		SB12	

The water quality monitoring data for each year was sorted by season: Wet season - November to April, and Dry season - May to October. The analysis includes precipitation years for three categories (Table 4-3): drought (1989-1992), normal (1993-1995), and wet 1996-1998). The data for each station for each season for the period of record has been summarized in Table 4-4a, b. The summary, which provides the expected environmental concentration (EEC) for the AERAP analysis, includes the number of samples, minimum concentration measured, maximum concentration measured, the mean and the standard deviation.

Table 4-3 Precipitation Classification

1989-1992	Drought
1993-1995	Normal
1996-1997	Wet
1998	Wet

The accumulated data is an adequate characterization of the concentrations of dissolved copper that resident species are exposed to in South San Francisco Bay. It is important to note that the sampling frequency and the averaging period are inconsistent with the time period used for chronic toxicity tests. Daily fluctuations in ambient concentrations and the duration of concentrations are assumed to not be significantly different than those measured by the monitoring programs. It would require an intensive monitoring program to address this uncertainty.

## 4.2.3 Application of the Indicator to South San Francisco Bay

The AERAP was applied to the South San Francisco Bay resident species toxicity database to develop a cumulative frequency curve to estimate the percentage of potentially affected community taxa to concentrations of dissolved copper. The form and summary statistics for the logistic regression model are provided below where:

$$p = \alpha + \beta * ln(x) + E$$

	Alpha	S.E. of Alpha	Beta	S.E. of Beta	Root MSE
Copper	-5.8353	0.2820	3.0014	0.1407	0.3165

The output of the logistic regression aquatic community risk model for chronic effects of copper on San Francisco Bay species is illustrated in Figure 4-5. The x-axis is the range of copper concentrations from individual species toxicity tests. The y-axis is the cumulative frequency curve for interpolating the percent of taxa affected at any chosen copper concentration. It is possible to extrapolate from a chosen concentration on the x-axis to identify the percent of taxa affected at the selected concentration. This model is the basis of additional analyses that are presented in Sections 4 and 5 of this report.

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 $Table \ 4-4a$  The Expected Environmental Concentrations (µg/L) for Dissolved Copper during the Wet Season at the Water Quality Monitoring Stations used in the AERAP Analysis

Station ID	N =	Minimum	Mean	Maximum	SD
SBDA					
C-1-3	7	2.6	3.1	3.8	0.5
C-3-0	7	2.6	3.4	4.3	0.6
C-5-0	6	3.0	3.5	3.9	0.4
C-6-0	6	3.2	3.5	4.3	0.4
R-4	7	2.8	3.5	4.5	0.6
SB-4	6	1.4	3.0	4.0	0.9
SB-5	7	2.6	3.2	4.1	0.5
SB-6	6	2.4	3.3	4.0	0.5
SB-7	7	2.7	3.3	3.8	0.4
RMP					
BA-10	7	1.6	3.3	4.9	1.2
BA-20	8	1.8	2.9	5.0	1.0
BA-30	8	1.9	2.7	3.7	0.6
C-1-3	7	1.4	2.5	4.8	1.3
C-3-0	7	1.6	3.4	5.9	1.4
San Jose WER					
DBN	12	1.4	2.2	3.3	0.4
DBS	12	1.7	2.5	3.5	0.5
CC	12	2.0	2.7	4.1	0.7
South Bay					
SB01	19	1.4	1.9	2.4	0.3
SB02	18	1.5	2.0	3.4	0.5
SB03	18	1.3	2.2	3.2	0.5
SB04	18	1.6	2.5	3.2	0.5
SB05	18	1.5	2.3	3.6	0.6
SB06	17	1.5	2.1	3.2	0.5
SB07	17	1.5	2.3	3.4	0.5
SB08	19	1.5	2.2	3.1	0.4
SB09	19	1.5	2.2	3.1	0.4
SB10	20	1.6	2.4	3.9	0.6
SB11	13	1.2	1.9	3.2	0.6
SB12	15	0.9	1.5	2.5	0.4

Table 4-4b

The Expected Environmental Concentrations (μg/L) for Dissolved Copper during the Dry Season at the Water Quality Monitoring Stations used in the AERAP Analysis

Station ID	N =	Minimum	Mean	Maximum	SD
SBDA					
C-1-3	7	3.1	5.3	8.9	2.1
C-3-0	7	3.3	5.4	9.4	2.2
C-5-0	6	3.6	4.9	7.3	1.7
C-6-0	6	3.0	4.8	7.9	1.9
R-4	7	2.6	4.6	6.8	1.6
SB-4	6	2.6	3.8	6.3	1.3
SB-5	7	2.2	4.0	6.5	1.5
SB-6	6	2.2	4.5	7.0	1.7
SB-7	7	2.3	4.4	6.6	1.5
RMP					
BA-10	5	3.1	3.6	4.5	0.6
BA-20	7	2.5	3.3	4.4	0.6
BA-30	7	2.4	3.0	3.7	0.5
C-1-3	5	2.0	3.2	4.3	0.9
C-3-0	5	2.1	3.3	4.1	0.9
San Jose WER					
DBN	13	2.1	2.8	3.7	0.4
DBS	13	2.3	2.9	3.7	0.4
CC	13	2.5	3.4	3.9	0.4
South Bay					
SB01	22	2.6	3.0	3.6	0.3
SB02	20	2.3	3.1	4.2	0.5
SB03	20	2.6	3.3	4.1	0.4
SB04	19	1.7	3.0	4.3	0.9
SB05	21	1.6	3.2	3.9	0.6
SB06	21	2.6	3.4	4.3	0.5
SB07	22	1.8	3.3	4.2	0.6
SB08	22	2.9	3.4	4.4	0.4
SB09	22	2.4	3.3	4.2	0.4
SB10	22	2.9	3.6	4.6	0.4
SB11	14	1.0	1.9	3.4	0.7
SB12	13	0.9	1.7	4.4	0.9

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The AERAP is used to perform three different applications of the indicator:

- 1. Risk Evaluations to develop estimates of Environmental Risk Concentrations for dissolved copper at five specified levels of protection for community taxa.
- 2. Comparisons to ambient or expected environmental concentrations-EECs (Section 4.3.5) combines the AERAP and site-specific study indicates to evaluate the potential for impairment due to ambient concentrations of dissolved copper at 29 monitoring stations located in Lower South San Francisco Bay.
- 3. Risk Hypothesis Tests (Section 4.3.5) are used to conduct a statistical comparison of the distribution of a 95% ERC with EECs from the ambient monitoring network.

Additional variations of these 3 applications are also developed as lines of evidence in Section 5.

#### Risk Evaluation

The AERAP was used to conduct risk evaluations to estimate environmental risk criterion concentrations for dissolved copper at five specified levels of protection for community taxa. The risk evaluations determine the chronic environmental risk criterion for a specified level of protection to community taxa. That is, the model can be used to estimate the environmental risk criterion (i.e., concentration of dissolved copper) that is protective of a particular percentage of the community taxa from chronic or acute effects. The environmental risk criterion (ERC) is one measure of the value of the indicator.

EPA water quality criterion guidelines recommend that water quality standards be protective of 95 percent of the species present in the aquatic system and that any subsequent criterion must be protective of the most sensitive commercially or economically species measured (U.S. EPA 1994). Thus, the criterion is intended to be protective of all species within the database. Therefore, 5% was the highest chronic risk criterion for copper that was evaluated using the aquatic community risk model. It is important to note that the ERCs generated by the risk evaluations are based on laboratory conditions. That is the concentrations do not reflect any "apparent complexing capacity" that exists in Lower South San Francisco Bay. The results of the risk evaluations are included in Table 4-5 below.

Table 4-5
AERAP Risk Evaluations for ERCs to
Protect 95 % to 99% of Community Taxa

Risk Evaluation	μg/L
5% ERC	3.1
95% CI	1.3/4.8
4% ERC	2.6
95% CI	1.1/4.0
3% ERC	2.0
95% CI	0.9/3.2
2% ERC	1.5
95% CI	0.6/2.4
1% ERC	0.9
95% CI	0.3/1.4

One of the primary decisions regarding the use of this indicator is the selection of the ERC level that will be used in the assessment. Selecting an ERC of 5% estimates a concentration that is protective of 95% of the taxa in the cumulative frequency curve. Selecting 4% protects 96% of the taxa, up to 1% which protects 99%. It is not possible to generate an estimate to protect 100% of community taxa.

The following questions were addressed in selecting an ERC level for assessing impairment to Beneficial Uses and recommending an SSO for South San Francisco Bay.

• Does the resident species toxicity database include an adequate sample of organisms from South San Francisco Bay?

The resident species toxicity database includes 13 species that reside in San Francisco Bay. There are hundreds, if not thousands of species of organisms within the bay. However, the 13 species included are an adequate sample size for the statistical procedure (logistic regression), and to calculate meaningful upper and lower confidence intervals (95% and 5%).

• Does the resident species toxicity database include a wide range of trophic levels and ecological niches?

Table 4-1 San Francisco Bay Resident Species Toxicity Database includes the trophic level and summary of niches occupied by each organism. A wide range of trophic levels and ecological niches are represented. These include primary producers, plankton grazers, filter feeders, detritus feeders, and predators at several size scales. The database does not include top-level predators such as harbor seals or herons. However, these

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organisms have copper tolerances that are well outside the range expected of ambient conditions. The species included in the database also represent a wide range of niches including but not limited to: tidal and shallow water sediment dwellers, pelagic fish, bottom fish, and plankton.

• Does the database include the range of expected sensitivities to dissolved copper?

The database represents a small sample of the overall species in San Francisco Bay, but they are believed to represent the range from most sensitive to least sensitive.

• What percentage of these taxa are necessary for South San Francisco Bay to fully meet the designated Beneficial Uses?

This is a difficult question to resolve. Individual species are important, especially those that are rare or endangered. However, this issue is not simply a question regarding the loss of an individual species. Rather, the question considers the function of a species in maintaining designated Beneficial Uses. For example, what role do nitrogen fixing blue-green algae play in the sustainability of other species that are more closely associated with the Beneficial Use? There are no fixed criteria. The assessment team have relied on best professional judgement regarding the structure and function of the South San Francisco Bay ecosystem.

The project team selected the 5% ERC for use in the impairment assessment and for use in developing an SSO recommendation. The 5% ERC value of 3.1  $\mu$ g/L is equal to the effects range for the most sensitive species included in the resident species toxicity database (*Mytilus edulis* -- free floating larval life-stage  $-3.08 \,\mu$ g/L). Therefore, the 5% value also protects species above that, which includes other trophic levels and niches represented in the database. It is important to note that there is some evidence of blue-green algae, and some species of dinoflagellates and diatoms that are sensitive to concentrations of *free ionic copper* below the range of the 3.1  $\mu$ g/L of dissolved copper associated with the 5% ERC (*Brand, et al 1986*). However, a resident diatom (*Thalassiosira pseudonana*) has a reported sensitivity to copper of 5.0  $\mu$ g/L dissolved. The dinoflagellate (*Gymnodinium splendens*) has a reported sensitivity to dissolved copper of 20.0  $\mu$ g/L. This suggests that there are dinoflagellates that have sensitivities to dissolved copper well above the 5% ERC. The presence of cyanobacteria in Lower South San Francisco Bay indicated that they are not impaired by ambient concentrations of dissolved copper (see section 4.4.3). The 5% ERC of 3.1  $\mu$ g/L is therefore protective of all plants that are included in the National Toxicity Database.

#### 4.2.4 Uncertainties

To apply the AERAP required the use of certain assumptions and extrapolations that introduce some uncertainty into the analysis. Several of these assumptions and extrapolations are briefly described below:

• The extrapolation of laboratory toxicity tests to the field is an accepted but imperfect assumption often used in water quality studies. This extrapolation and studies being conducted to evaluate it are described in Section 3.1.1. For example, individual

- laboratory toxicity tests do not account for cumulative effects on resident species from other stressors (e.g., exotic species, other pollutants, and physical habitat limitations).
- What is the ecological importance of the 5% of species that could potentially be affected? Species believed to be within the potentially impacted range include Cyano bacteria (blue-green algae) and possibly some species of dinoflagelates. How important are these species in the food chain and therefore to maintaining basic ecological integrity in South Bay? Information from the plankton indicator can be useful in helping to address this issue.
- How well does the water quality monitoring database characterize the conditions
  resident organisms are exposed to? The water quality concentrations used in the risk
  analyses summarize (i.e., mean, minimum, maximum, standard deviation) of samples
  taken within a season. The assumption is that the water quality data summaries are
  consistent with an analysis for chronic effects and that the database adequately
  characterizes exposures to resident organisms.

## 4.2.5 Resolving Key Uncertainties

The following list of studies are possibilities not necessarily recommendations.

## **Extrapolation of laboratory toxicity testing results to the field:**

- The Water Environment Research Foundation recently completed a study that
  evaluates the ability of whole-effluent toxicity tests (WET) to predict effects within
  the receiving water body (Diamond et al 1997). The study concludes that the WET
  methodology, which approximates the laboratory procedures, effectively estimates the
  impacts of discharges on receiving waters.
- The results of the site-specific studies described in Section 4.3 help to address the
  uncertainties associated with the extrapolation of laboratory toxicity tests to South
  San Francisco Bay.
- In-situ toxicity tests would represent the highest level of validation for the resident species toxicity database. In-situ tests would be expensive and time consuming and is not be recommended unless stakeholders have significant concerns after consideration of the information included above.

#### **Ecological importance of 5% of species potentially impacted:**

- Expand the resident species toxicity database to include more species to better characterize the distribution of sensitivities of resident organisms.
- Continue to monitor status of benthic macroinvertebrates in South Bay as a check on the ability of toxicity tests and the viability of the 5% ERC estimated by the AERAP. Effects on the benthic macroinvertebrate community cannot be directly linked to copper. A finding of negative impact should be used as a trigger for additional

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- evaluation of the 5% ERC. However, if the measures of community status indicate no impact this could be used to verify the 5% ERC.
- Convene workshop of estuary ecologists to consider the recommended 5% ERC to better evaluate the role of potentially impacted species in sustaining Lower South San Francisco Bay Beneficial Uses.

## Adequate characterization of exposure conditions to resident species:

• Supplemental water quality monitoring studies could be conducted to better characterize the spatial and temporal variability associated with dissolved copper concentrations in South San Francisco Bay.

#### 4.2.6 Results - Contribution of the Indicator to the Assessment

The AERAP analysis of the Resident/Surrogate species toxicity database provides the basis for estimating a 5% chronic ERC for dissolved copper for South San Francisco Bay of 3.1  $\mu$ g/L. The proposed ERC compares to the National Toxics Rule dissolved copper concentration of 3.1  $\mu$ g/L. The proposed ERC has the advantage of being developed from a toxicity database of species resident to San Francisco Bay.

The results of this indicator will be combined with others in later sections of this report to evaluate impairment assessment and to develop a recommended SSO.

# 4.3 Site-Specific Studies Indicator

The previous two indicators use the response of aquatic organisms in laboratory water to copper and nickel to generate a water quality criterion. These indicators produce criteria that are potentially over-protective of the beneficial uses of Lower South San Francisco Bay because they do not consider the effects of ambient water quality characteristics. The Site-Specific Studies Indicator is defined as the response of resident aquatic organisms to copper and nickel in ambient Lower South San Francisco Bay water. This response can be measured or predicted using procedures described by Carlson, et al. (1984) and the proposed NTR (U.S EPA, 1997) that allow the national criteria to be modified so that they more accurately reflect ambient conditions and metals bioavailability. This modification procedure can be used in either of three ways:

- **Recalculation Procedure** This procedure allows modifications to the national data set by eliminating data for species that are not residents. It is designed to account for any real difference between the sensitivity range of species represented in the national data set and those found locally.
- Indicator Species Procedure This procedure allows for modifications to the national criterion by using a site-specific multiplier, which accounts for ambient water quality characteristics that may affect the bioavailability of copper and nickel.

 Resident Species Procedure - This procedure allows for modification of the national criterion by concurrently testing resident species for chronic and acute toxicity in ambient site water.

Site-specific studies that use ambient Lower South San Francisco Bay water and resident species provide an estimate of the amount of copper and nickel that is bioavailable. Thus allowing for a site-specific water quality objective that is fully, yet not overly, protective of the beneficial uses of Lower South San Francisco Bay. These studies:

- Provide a measure of local water quality characteristics that can either mitigate or enhance the toxicity of dissolved copper and nickel - known as the apparent complexing capacity. Apparent complexing capacity provides an important buffering component to the ecosystem and can reduce the toxic effects of pollutants like copper and nickel on resident organisms. The apparent complexing capacity is composed of natural and anthropogenic compounds (organic ligands and man-made chelators) and ions (e.g., manganese and iron) which compete with copper and nickel for binding sites on or in the organism;
- Take into account the interactions between copper and nickel and the myriad of other compounds or chemicals that are present in Lower South San Francisco Bay. These compounds may 1) increase the toxicity of copper and nickel to an organism (synergism) (i.e., copper and nickel are more toxic to an organism when these compounds co-occur than when they don't), 2) decrease the toxicity of copper and nickel to an organism (antagonism) (e.g., ionic competition) and 3) add to the toxicity of copper and nickel to an organism (additivity) (e.g., some metals behave in an additive fashion where their individual concentrations aren't high enough to be toxic to aquatic organisms, but when added together become toxic); and
- Allow for resident rather than non-resident species to be used to determine local water quality objectives.

The results of the site-specific studies are used to determine whether current national water quality criteria are over-protective of the beneficial uses, and therefore, inappropriate for Lower South San Francisco Bay.

This section provides 1) an historical perspective of site-specific studies; 2) a description of how the Site-Specific Studies Indicator can be used to modify the national water quality criterion so that they more accurately reflect local water quality characteristics; and 3) a review of some site-specific case studies that have been performed in both San Francisco Bay and Lower South San Francisco Bay.

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## 4.3.1 Site-Specific Studies, an Historical Perspective

The U.S. EPA first set standards for metal discharges to water in the mid-1980s. These standards were based on the toxicological response of aquatic organisms. The responses were measured using standardized bioassay tests in which the test organisms were exposed to single metals in laboratory water for a given period of time. These test endpoints were expressed as the concentration of "total" metal that adversely affected an organism's survival, growth, or reproduction. Subsequent water quality criteria were based on those values.

The state of knowledge of how aquatic chemistry affects metal speciation and toxicity to aquatic organisms has advanced considerably over the last 15 years. In the mid-1980s, there was minimal understanding of either the importance of metal speciation in natural waters or the mechanisms of metal toxicity to aquatic organisms. Scientists knew that chemistry affected the bioavailability of metals to aquatic organisms and that metal toxicity in ambient waters can differ significantly from water toxicity in the laboratory. This was because several variables (e.g., temperature, pH, salinity, suspended solids, organic carbon, and competitive ions) that occurred in ambient water were either not present, or were closely controlled under laboratory conditions. But aquatic chemists said that differentiating the amount of bioavailable metal from the amount of total metal was much too complicated, so the decision was made to use the conservative approach and assume that all of the metal was bioavailable (Renner 1997). By the late 1980s to early 1990s, aquatic toxicologists considered the dissolved fraction of metals to be more bioavailable than the total fraction and, the U.S. EPA (Prothro, 1993) issued guidelines that allowed for using dissolved metal concentrations to set water quality criteria. This guidance states that criteria that were based on total metal concentrations were most likely overprotective of aquatic organisms and their uses.

Criteria that were based on dissolved metals concentrations only provided a first step toward being able to understand how aquatic organisms respond to toxicants in ambient conditions. The next step was to compare an organism's response to a toxicant using ambient water to the national criterion for that toxicant and make adjustments to the national criterion, if needed. Even though methods describing how the national water quality criteria could be modified to reflect ambient water quality characteristics and resident species' sensitivities have been in the guidelines since 1983, most water quality criteria were used without consideration of site-specific conditions. These procedures include using resident species and ambient site-water to determine a local site-specific water quality criterion and are discussed in the following section.

## 4.3.2 Methods Used to Modify the National Water Quality Criterion

Site-specific modifications (Carlson, et al. 1984) to the national water quality criteria provides a more comprehensive mechanism for addressing the bioavailability of metals to aquatic organisms than simply looking at the dissolved metals fraction. Consequently, criteria expressed solely in terms of dissolved metal concentrations does not account for the effects of organic ligands or competitive inorganic ions on metals bioavailability and subsequent toxicity (this is particularly true for copper which forms reduced-toxicity complexes with dissolved organic matter). It also does not account for the sensitivities of resident species to metals. The methods that are used to modify the national water quality criterion take these issues into consideration and provide a site-

specific water quality criterion that is fully protective of beneficial uses, while not being overprotective. There are several requirements and three procedures (i.e., Recalculation, Indicator Species, and Resident Species) that form the basis of the site-specific criterion calculation modification. These requirements and procedures are described in the following sections.

## **Site-Specific Criterion Requirements**

- 1. Acceptable test results using at least one saltwater animal in at least eight different families such that all of the following are included:
  - Two families in the phylum Chordata;
  - Family in a phylum other than Arthropoda or Chordata;
  - Either the Mysidae or Penaeidae family;
  - Three other families not in the phylum Chordata (may include Mysidae or Penaeidae, whichever was not used above); and
  - Any other family.
- 2. Acute-to-Chronic Ratios with species of aquatic animals in at least three different families provided that of the three species, at least one is:
  - A fish:
  - An invertebrate; and
  - An acutely sensitive saltwater species (the other two may be freshwater species).
- 3. Results of at least one acceptable test with a saltwater alga.
- 4. At least one acceptable bioconcentration factor determined with an appropriate saltwater species, if a maximum permissible tissue concentration is available.

If all of the required data are available, a criterion can be calculated. The procedures for calculating a site-specific criterion are presented below.

**Recalculation Procedure -** This procedure allows modifications in the national data-set by eliminating data for species that are not local residents and is designed to account for any differences between the sensitivity range of species represented in the national data-set and the sensitivity of the resident species. If, after eliminating the non-native species, the resulting data-set does not meet the minimum requirements for recalculation, additional acute testing using appropriate resident species would be required. No chronic testing would be necessary since the Final Acute-to-Chronic Ratio would be used to calculate the site-specific Final Chronic value.

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The recalculation is accomplished by using the following sequence:

- Calculate the Species Mean Acute Values (SMAV) by taking the geometric mean of the response of all acute endpoints that use the same species and dilution water;
- Calculate the Genus Mean Acute Value (GMAV) by taking the geometric mean of the SMAVs that are from organisms within the same genus;
- Rank the GMAVs from high to low and assign the lowest GMAV the number "1" and the highest GMAV the number "n";
- Select the four GMAVs which have cumulative probabilities closest to 0.05 (if less than 59 GMAVs are used, then these will always be the lowest four GMAVs);
- Calculate the site-specific Final Acute Value (FAV) by performing a modified regression analysis on the GMAVs (see Stephan, et al. 1985 for equation);
- The site-specific maximum concentration (CMC) is then calculated by dividing the FAV by 2 (i.e., FAV  $\div$  2 = CMC);
- Divide the site-specific FAV by the national Final Acute-to-Chronic Ratio (FACR) to obtain the site-specific Final Chronic Value (FCV) (i.e., FAV ÷ FACR = FCV); and
- The Final Chronic Value (FCV) becomes the Criterion Continuous Concentration (CCC).

If these values are significantly different from the national criterion, they can be implemented and used as a site-specific water quality criterion.

Indicator Species Procedure - This procedure is based on the assumption that the physical and/or chemical characteristics of ambient water may influence the bioavailability and toxicity of a pollutant. Acute toxicity in site water and laboratory water is determined concurrently using either resident species, or acceptable non-resident species which are used as surrogates for the resident species. The difference in toxicity values, expressed as a Water Effects Ratio (WER), is used to convert the national maximum concentration for a pollutant to a site-specific maximum concentration from which a Final Acute Value is derived (as long as the WER value is significantly different from 1). A site-specific Final Acute-to-Chronic Ratio can be calculated by using this procedure when ambient water quality characteristics makes using the national Final Acute-to-Chronic Ratios inappropriate.

This procedure provides three ways to obtain a site-specific Final Chronic Value (FCV). This value may be:

Calculated (no testing required) if an applicable Final Acute-to-Chronic Ratio for a
given material is available in the national criteria document. This ratio is simply
divided into the site-specific Final Acute Value to obtain the site-specific Final
Chronic Value,

site-specific FAV ÷ FACR = site-specific FCV;

Obtained by performing two acute and chronic toxicity tests including both a fish and
invertebrate species (resident or non-resident) in ambient water. Acute-to-Chronic
Ratios (ACRs) are calculated for each species, and the geometric mean of these ratios
is then divided into the site-specific Final Acute Value (FAV) to obtain the sitespecific Final Chronic Value (FCV),

site-specific FAV ÷ site-specific ACR = site-specific FCV; or

- Obtained by performing chronic toxicity tests with at least one fish and one invertebrate (resident or non-resident) in both laboratory and ambient water and calculating a geometric mean of the chronic Water Effects Ratios. This value is then used to modify the national Final Chronic Value using the following steps,
- 1. chronic endpoints in ambient water ÷ chronic endpoint in lab water = chronic WER;
- 2. geometric means of WERs = final site-specific chronic WER (FWER); and
- 3. FWER national water quality criterion = site-specific FCV.

If these values are significantly different from the national criterion, they can be implemented and used as a site-specific water quality criterion.

**Resident Species Recalculation Procedure -** This procedure is used to account for differences in resident species' sensitivity and differences in bioavailability and toxicity of a material due to variability in the physical and chemical characteristics of the ambient water. This procedure is designed to compensate concurrently for differences between the sensitivity range of species represented in the national data-set and for site water which may markedly affect the bioavailability and toxicity of the material of interest.

This procedure requires that the complete acute toxicity minimum data set be developed using ambient water and resident species only. The minimum data-set requirements are detailed earlier in this section.

The site-specific Final Acute Value is calculated in the same manner that is used in the Recalculation Procedure and the site-specific Final Chronic Value is calculated in the same manner that is described in the Indicator Species Procedure.

The Resident Species Procedure may require a rather extensive number of toxicity tests on resident species for the derivation of site-specific criteria. As a result, this procedure has rarely been employed for the derivation of site-specific criteria.

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## 4.3.3 Site-Specific Case Studies for San Francisco Bay and Lower San Francisco Bay

The U.S. EPA (1984) established national water quality criteria for total copper and nickel to be 2.9 µg/L and 8.3 µg/L, respectively. Regulators used these criteria to set local water quality objectives for San Francisco Bay. In 1995, the U.S. EPA recommended that dissolved instead of total metals concentrations be used to determine water quality criteria and changed the national saltwater quality criterion for copper from 2.9 µg/L (total copper) to 3.1 µg/L (dissolved copper). This caused the WER value of 1.7 that was calculated using the values that were obtained from the SFRWQCB study (S.R. Hansen & Associates, 1992a) and the validity of the resultant site-specific water quality criterion for copper of 4.9 µg/L to be questioned since the original values were based on total copper and the new criterion was based on dissolved copper. The U.S. EPA Guidelines (Stephan, et al., 1985) state that, "criteria must be used in a manner that is consistent with the way in which they were derived if the intended level of protection is to be provided in the real world."

To better characterize the effects of ambient water quality conditions on the toxicity of copper and nickel to aquatic organisms, the procedures described by Carlson, et al. (1984) have been used (Larry Walker et al., 1991a, b; S.R. Hansen & Associates, 1992a, b; Watson, et al., 1996, 1999; and the City of San Jose, 1998) several times between 1991 and 1998 to:

- Assess the resident species' sensitivity to copper and nickel and ambient water quality characteristics of San Francisco Bay and Lower South San Francisco Bay; and
- Determine whether or not a site-specific water quality criterion for copper and nickel would be justified for San Francisco Bay and Lower South San Francisco Bay.

Each of these studies (Larry Walker et al., 1991a, b; S.R. Hansen & Associates, 1992a, b; Watson, et al., 1996, 1999; and the City of San Jose/Santa Clara Water Pollution Control Plant, 1998) have indicated that San Francisco Bay and Lower South San Francisco Bay have water quality characteristics that made copper and nickel up to an order of magnitude less toxic to aquatic organisms than was predicted by the national water quality criteria.

The results from all available site-specific studies performed on the San Francisco Bay and Lower South San Francisco Bay have been included in this assessment in order to present a comprehensive set of data and to provide an historical context to previous site-specific water quality objectives for the San Francisco Bay region. These case studies are summarized in chronological order in the following sections.

## 4.3.3.1 Cities of San Jose and Sunnyvale NPDES E5E Site-Specific Studies

Larry Walker Associates, et al (1991a, b) performed copper and nickel site-specific studies in Lower South San Francisco Bay between February and June, 1991 for the Cities of San Jose and Sunnyvale. These studies were required by their NPDES permits and provided information that the San Francisco Regional Water Quality Control Board needed before they could set a site-specific water quality objective for both copper and nickel for Lower South San Francisco Bay.

Selection of sampling sites within Lower South San Francisco Bay was based on the following:

1) topographical and hydrodynamic characteristics of the Lower South San Francisco Bay, 2) site water physicochemical characteristics, and 3) the "zone of influence" created by the discharge of municipal wastewater. Based on these criteria, a "regional" site was chosen. This study region ranged from a station just north of the Dumbarton Bridge to just west of the mouth of Coyote Creek at USGS station 36. A regional approach was selected as the sampling "site" to provide flexibility in acquiring site water samples. In addition, this region would:

- Be representative of the open basin region of the Lower South San Francisco Bay;
- Be representative of the "upstream" or saltwater source of the Lower South San Francisco Bay (Central San Francisco Bay); and
- Be least affected by the municipal wastewater discharged into the southern portion of the Lower South San Francisco Bay.

They calculated copper WER values that ranged from 1.36 to 7.03 using a fish, *Menidia beryllina* and a bivalve, *Mytilus edulis* as test organisms. Based on these results, Larry Walker Associates, et al. (1991a, b) recommended a total copper CCC value of 14.0 µg/L for Lower South San Francisco Bay.

The same study calculated nickel Acute-to-Chronic Ratios using a fish, *Menidia beryllina* and a mysid shrimp, *Mysidopsis bahia* that ranged from 1.29 to 6.91. Based on these results they recommended that the nickel criterion for Lower South San Francisco Bay be set at 9.9 µg/L, based on total nickel. This study is discussed in greater detail in the following sections.

Copper - Larry Walker Associates, et al. (1991a, b) used the Indicator Species Procedure to derive a saltwater site-specific water quality criterion for copper for Lower South San Francisco Bay. This procedure was selected over the other site-specific procedures (Recalculation and Resident Species Procedure) because the researchers felt that the method accounted for the site-specific chemistry of Lower South San Francisco Bay. In addition, the species present in the Lower South San Francisco Bay appeared to be adequately represented by the national criteria data-set. Of the three options that are outlined for derivation of site-specific criterion using the Indicator Species Procedure (Carlson, et al. 1984), the WER method was selected because previous studies had indicated that the acute toxicity of copper in Lower South San Francisco Bay water was lower than in laboratory water.

Five observations can be made from the results obtained from the lab and site-water toxicity tests (Table 4-6):

- Site-specific WERs for both *M. edulis* and *M. beryllina* were significantly greater than 1.0 during each of the four test events;
- The *M. edulis* WERs were always greater than the *M. beryllina* WERs;

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- The WERs for the two species were not significantly different from each other during the February-March sample event;
- *Mytilus edulis* was always at least an order of magnitude more sensitive to copper than was *M. beryllina*; and
- ambient copper concentrations were always well below the site-water EC50 value for *M. edulis*, with the average ambient total copper concentrations being 4 times less than the geometric mean of the *M. edulis* EC50 values.

Mytilus was used to calculate the site-specific copper criterion because it was more sensitive to copper than M. beryllina. The site-specific water quality criterion for copper was calculated by taking the product of the national water quality criterion for copper (2.916) and the arithmetic mean of the M. edulis WERs (4.79) to yield 14.0 µg/L (based on total copper).

**Nickel -** Larry Walker Associates, et al. (1991a, b) used the **Indicator Species Procedure** to derive a saltwater site-specific water quality criterion for nickel for Lower South San Francisco Bay. Of the three options that are outlined for derivation of site-specific criterion using the Indicator Species Procedure (i.e., WER method, Site-Specific Acute-Chronic Ratio method, and Site-Specific Chronic Value method) (Carlson, et al. 1984), this study employed the Site-Specific Acute-Chronic Ratio Method to derive the site-specific water quality criterion for nickel. This method of the Indicator Species Procedure was selected because the national acute-chronic ratio for nickel was based on only one saltwater species: *Mysidopsis bahia* (U.S. EPA 1986). Therefore, the authors state, "the derivation of a site-specific criterion is appropriate in lieu of the small saltwater database used in the derivation of the national acute-chronic ratio for nickel."

The authors of this study believed that a site-specific criterion for nickel in Lower South San Francisco Bay was warranted because the national nickel ACR (17.99) which is composed of two freshwater ACRs (29.86 and 35.6) and one saltwater ACR (5.478) was more than three times larger than the single saltwater ACR. In addition, Larry Walker associates, et al (1991a, b) states that, "using the national nickel ACR produces a saltwater criterion for nickel which is substantially lower than any reported acute or chronic toxicity value for nickel."

Table 4-6	
Summary of Acute Toxicity Test Results for Copper and Calculated WER	s

Species		c/LC <sub>50</sub> otal copper)	Ambient Copper Concentration (µg/L as total copper)	
	Lab water	Ambient water	WER	
February 14-21, 1991				
Mytilus edulis	8.9	27.2	3.05	6.3
Menidia beryllina	115.4	156.7	1.36	
February 27 - March 6				
Mytilus edulis	8.2	35.1	4.29	6.6
Menidia beryllina	63.0 - 96.5*	204	2.11 - 3.24	
April 2 - 9				
Mytilus edulis	8.3	58.3	7.03	15.2
Menidia beryllina	123	>335.2	>2.72	
May 29 - June 1				
Mytilus edulis	not tested due to poor spawning success			10.1
Menidia beryllina	131	>330.1	>2.52	

(Adapted from: Larry Walker Associates, et al. 1991a, and b)

A fish (*M. beryllina*) and an invertebrate mysid shrimp (*M. bahia*) were the test organisms that were used in this study. They were selected because they were the most sensitive species in the national data-set to nickel. Test results (Table 4-7) indicated that.

- *Mysidopsis bahia* was much more sensitive to nickel than *M. beryllina* (both acutely and chronically) and
- The geometric mean of the individual calculated ACRs for *M. bahia* (>2.59) was greater than the geometric mean of the calculated ACRs for *M. beryllina* (1.78).

An examination of the national criterion data-set indicated that there were some toxicity values missing. When these values were added to the data-set, the national FAV was re-calculated, replacing the original FAV of 149.2  $\mu$ g/L with a new FAV of 177.4  $\mu$ g/L. This re-calculation also resulted in changing the national CMC from 74.6 to 88.7  $\mu$ g/L. The revised national Final Chronic Value (FCV) was calculated as the quotient of the new national FAV (177.4  $\mu$ g/L) and the national ACR (17.99) and yielded a national chronic value of 9.9  $\mu$ g/L. Since the national CCC was equal to the Final Chronic Value, they recommended that the national CCC be changed to 9.9  $\mu$ g/L to reflect the additional data.

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<sup>\*</sup> Range was dependent on statistical calculation procedure.

Table 4-7
Summary of Acute and Chronic Nickel Toxicity Results for *M. beryllina* and *M. bahia* and Calculated ACR Values

Species	Acute (LC <sub>50</sub> μg/L)		Chronic EC50 Concentration in Site Water (µg/L)Site Water	Acute- ChronicRatio (ACR)
	Lab Water	Site Water		
M. bahia*	508		92.7 (lab water)	5.48
M. beryllina*	38,000			
Feb. 14-21, 1991				
M. bahia	916	916	583	1.57
M. beryllina	16,834	19,216	13,006	1.48
Feb. 27- March 6				
M. bahia	636	>912	580	>1.57
M. beryllina	19,400	22,280	13,004	1.71
April 2-9				
M. bahia	615.4	784	297	2.64
M. beryllina	15,500	15,160	5,317	2.85
May 29-June 1				
M. bahia	951	1,080	156	6.91
M. beryllina	18,110	25,420	18,385	1.38

<sup>\*</sup> From: U.S. EPA (1986) Ambient Water Quality Criterion Document for Nickel Data from: Larry Walker Associates, et al. (1991a, b)

# 4.3.3.2 San Francisco Bay Regional Water Quality Control Board Site-Specific Copper and Nickel Studies

This study performed by S.R. Hansen & Associates (1992a, b) for the San Francisco Bay Regional Water Quality Control Board (SFRWQCB) used the Water Effects Ratio method of the Indicator Species Procedure to calculate a site-specific water quality criterion for copper and nickel for San Francisco Bay. This study was performed between May and October, 1991, encompassed six sites within San Francisco Bay, and indicated that all portions of San Francisco Bay contained some metal-complexing ability. This metal-complexing ability reduced copper and nickel toxicity to aquatic organisms with the greatest amounts of metal-complexing occurring at the extreme ends of the Bay (i.e., Lower South San Francisco Bay and San Pablo Bay) and lesser amounts occurring in the central areas of San Francisco Bay. S.R. Hansen & Associates used the differential pulse anodic stripping voltammetry-hanging mercury drop electrode (DPASV-HMDE) to measure labile copper in the test solutions. This method has been validated by Donat, et.al. (1994).

Bay-wide Water Effects Ratios were calculated for total copper using the oyster, *Crassostrea gigas* and the diatom *Thalassiosira pseudonana*. These WER values ranged from 2.1 to 6.1 and were used to calculate a Bay-wide copper criterion of 4.2 µg/L (as dissolved copper). The nickel

study provided a single WER value of 9.3 based on the response of the urchin, *Lytechinus pyctus*. The details of these individual studies are presented in the following sections.

**Copper -** The oyster, *Crassostrea gigas* and the diatom, *Thalassiosira pseudonana* were the test species that this study used to calculate the WERs that were used to calculate a site-specific copper criterion for San Francisco Bay. Bay-wide WERs ranged from 2.1 for *C. gigas* to 6.1 for *T. pseudonana* and were based on total copper. Water Effects Ratios using only the two Lower South San Francisco Bay sites were 1.5 for the *C. gigas* and 6.2 for *T. pseudonana* and were greater for both species than the WERs that were observed in the central portion of San Francisco Bay (Table 4-8).

Table 4-8
Summary of Mean WERs in Ambient Waters of San Francisco Bay

		Water Effe	ects Ratios	
Station	C.gigas		T. ps	seudonana
	NOEC <sup>1</sup>	Chronic value <sup>2</sup>	NOEC	Chronic value
	2.1	2.4	5.6	4.9
Dumbarton Bridge	1.2	1.3	7.1	7.8
San Mateo Bridge	1.2	1.4	2.0	1.2
South Central Bay	1.6	1.4	5.6	4.4
Central Bay	2.0	1.7	6.0	4.0
San Pablo Bay	4.0	4.1	13.9	>10.4
Mean	2.0	2.1	6.7	5.5
Geometric Mean of NOEC and Chronic Value WER Means	2.1			6.1

From: S.R. Hansen & Associates (1992a)

- 1 No Observable Effect Concentration (NOEC) is the highest test concentration that exhibits no observed toxicological effect.
- 2 Chronic value = Geometric Mean of the No Observable Effect Concentration and lowest Observable Effect Concentration. The Lowest Observable Effect Concentration (LOEC) is the lowest test concentration that exhibits a toxicological effect.

These results would support the development of a regional criterion for copper, with special emphasis on the Lower South San Francisco Bay and San Pablo Bay. However, when the authors looked at the minimum chronic values, they noticed that, on occasion, even the extreme portions of San Francisco Bay (i.e., Lower South San Francisco Bay and San Pablo Bay) had lower copper complexing capacity and greater toxicity than did the central portions of San Francisco Bay. This suggested that regional criteria may not be appropriate and, based on this conflicting evidence, the authors could see no clear rationale for deriving regional site-specific criteria for copper (based on the available information) and a Bay-wide site-specific copper objective was recommended.

The site-specific Final Acute Value was calculated by using the geometric mean of the *C. gigas* and *T. pseudonana* WER values to obtain a Final Water Effects Ratio (FWER) and multiplying the FWER by the national FAV for copper. This produced a site-specific FAV of 20.9  $\mu$ g/L.

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Dividing the site-specific FAV by the national ACR (2, when a bivalve larval test is used) produced a site-specific Final Chronic value (FCV) of 10.4 µg/L (as total copper).

This site-specific FCV of 10.4 was determined to be generally protective, however, on one occasion, an adverse impact was observed during this study at a lower copper concentration (7.2  $\mu$ g/L for *T. pseudonana* at the Central Bay station). Because of this, the lowest of the two WER values (i.e., 2.1 for *C. gigas*) was used. This approach produced a site-specific FAV of 12.2  $\mu$ g/L and a site-specific FCV of 6.1  $\mu$ g/L. This site-specific FCV was protective of the lowest chronic value observed (i.e., 7.3  $\mu$ g/L for *T. pseudonana* in Central Bay and 14.8  $\mu$ g/L for *C. gigas* in South Central Bay). The calculated criterion was determined to be well below both of the observed chronic values.

To avoid the possibility that total copper concentrations in San Francisco Bay would increase when suspended solids concentrations increased, and therefore possibly causing the total copper concentrations to exceed the site-specific criterion, the study proposed basing the criterion on dissolved concentrations of copper. The proposed site-specific criterion for copper in San Francisco Bay was based on the lowest chronic value observed in the study  $(4.2 \,\mu\text{g/L} \text{ as dissolved copper for } \textit{T. pseudonana})$ .

The San Francisco Regional Water Quality Control Board (SFRWQCB) used the results of this study to propose a site-specific total copper WER value of 1.7 and the Basin Plan was amended to replace the national copper water quality criterion of 2.9  $\mu$ g/L with a site-specific total copper water quality objective of 4.9  $\mu$ g/L (i.e, 2.9  $\mu$ g/L X 1.7 = 4.9  $\mu$ g/L).

**Nickel -** In September and October of 1992, S.R. Hansen & Associates (SRH&A) used the Water Effects Ratio method of the **Indicator Species Procedure** to 1) determine whether a site-specific criterion for nickel in Lower South San Francisco Bay was warranted, 2) if so, develop the site-specific criterion for nickel and 3) to determine the toxicologically significant concentration of nickel in ambient waters.

This study was preliminary and not all of the objectives were met. S.R Hansen & Associates (1992b) screened 11 species (2 fish, 3 algal, and 6 invertebrates) to determine the most sensitive species to nickel in laboratory water. Their results indicated that two species both invertebrates, (oyster, *Crassostrea gigas* and the white urchin, *Lytechinus pyctus*) proved to be the most sensitive of the 11 species that were tested for nickel.

Limited resources and spawning failures meant that each of the two species could be tested only once and not simultaneously. Toxicity tests were performed using ambient water collected from two sites in Lower South San Francisco Bay. One site was located approximately 2-3 miles south of the Dumbarton Bridge and the second site was located approximately 300 feet south of Dumbarton Bridge.

Water Effects Ratios were calculated for each test organism and site water after each sampling event (Table 4-9). These results indicated that nickel toxicity to the urchin, *L. pyctus* was less in ambient site waters than in laboratory water for both Lower South San Francisco Bay sites. In contrast, the oyster, *C. gigas* exhibited WERs very close to 1.0 and, therefore, there was no

difference between nickel toxicity to *C. gigas* in either ambient site waters or laboratory water. This was probably an artifact of the relative sensitivities of each of the species to nickel, with the oyster being between one and two orders of magnitude less sensitive to nickel than the urchin. It is generally accepted that greater WER values are obtained from species that are more sensitive to a toxicant than from species that are less sensitive.

Table 4-9
Summary of Nickel WERs Developed for South San Francisco Bay using *C.gigas* and *L. pyctus* (Based on Total Nickel)

Site	Crassostrea WERs		Lytechi	nus WERs
	NOEC	Chronic value	NOEC	Chronic value
Dumbarton	0.8	0.9	13.0	5.1
South Bay	0.8	0.9	43.3	17.1
Geometric Mean	0.8	0.9	23.7	9.3

From: S.R. Hansen & Associates (1992b)

The results from this preliminary test indicated that, at least during the study period, a site-specific criterion for nickel in Lower South San Francisco Bay was most likely warranted. They based this conclusion on the average WER value of 9.3 that was obtained from the urchin, *L. pyctus*.

# 4.3.3.3 City of San Jose/Santa Clara Recalculation of the Nickel National Criterion and Site-Specific Studies

The City of San Jose (Watson, et al. 1996; 1999) used a combination of the **Species Recalculation** and **Indicator Species Procedures** to update the national data-set and calculate a site-specific Final Acute-to-Chronic Ratio and a site-specific water quality criterion for nickel for the Lower South San Francisco Bay.

In 1995, Watson, et al. (1996) recalculated the numeric nickel national water quality criterion using the procedure outlined by the U.S. EPA (Carlson, et al. 1984). The corrections, additions, and deletions resulted in a proposed criterion of  $10.2 \,\mu\text{g/L}$  using the most conservative approach.

During this recalculation process, it became obvious that there were no recent chronic data that could be used to recalculate the Final Acute-to-Chronic Ratio (FACR). The FACR derived in 1986 (17.99) was based on two freshwater and one marine species. There was a large difference between the freshwater and saltwater ACR values that contributed to the FACR. The ACR for the freshwater minnow, *Pimephales promelas*, was 35.58 and that for the waterflea, *Daphnia magna*, was 29.86. Only one marine species, the mysid shrimp, *Mysidopsis bahia* (since reclassified as *Americamysis bahia*), had verifiable chronic data upon which to base an ACR value of 5.48.

In 1997, Watson, et al. (1999) designed acute and chronic flow-through bioassay tests on three marine species (topsmelt fish, *Atherinops affinis*; red abalone, *Haliotes rufescens*; and the mysid

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shrimp, *Mysidopsis intii*). The topsmelt is a native to Lower South San Francisco Bay, while the other two species are West Coast natives and commonly used surrogate species. The chronic endpoints were:

- Topsmelt larval hatching, survival, and growth after an exposure period of over 40 days,
- Abalone metamorphosis and juvenile growth after an exposure period of over 22 days, and
- Mysid survival, growth, and brood size/fecundity after an exposure period of over 28 days.

Watson, et al (1996, 1999) updated the national data-set by deleting non-native species, eliminating questionable data from the data set, adding additional saltwater acute and chronic test data to the dataset, and recalculating a new "proposed" national and site-specific criterion for nickel. Abalone and mysids were far more sensitive to nickel than was topsmelt. Chronic values for abalone and mysids were similar (26.43 and 22.09  $\mu$ g/L, respectively), and were lower than available literature values. The chronic value for the topsmelt was 4,270  $\mu$ g/L. Since abalone is a commercially important species, the calculated Final Acute Value (FAV) was replaced by the lower abalone Final Acute Value (145.5  $\mu$ g/L) in order to protect this species.

The recalculated national and South San Francisco Bay site-specific FAVs were 145.5  $\mu$ g/L and 124.8  $\mu$ g/L, respectively, with the FACR being either 10.50 (using a combination of freshwater and marine ACRs) or 5.959 (Using only the four marine species' ACRs). Using these values, Watson, et al (1996, 1999) was able to justify that a new national and site-specific criterion for nickel be set at 13.86 and 11.89  $\mu$ g/L, respectively when the freshwater and marine combined ACR was used (equations 1 and 2). Watson et al. (1996; 1999) also calculated national and Lower South San Francisco Bay site-specific nickel criteria of 24.42 and 20.94  $\mu$ g/L, respectively using the marine ACR (equations 3 and 4):

```
Formula: FAV \div ACR = CCC

Equation 1 145.5 \mug/L \div 10.50 = 13.86 \mug/L,

Equation 2 124.8 \mug/L \div 10.50 = 11.89 \mug/L,

Equation 3 145.5 \mu g/L \div 5.959 = 24.42 \mug/L,

Equation 4 124.8 \mug/L \div 5.959 = 20.94 \mug/L.
```

Acute-to-chronic ratios for all three marine species were remarkably similar, ranging from 5.50 to 6.73. These values were comparable to the ACR value previously reported for *M. bahia* of 5.48 (U.S. EPA 1986). A FACR derived solely from a geometric mean of these four marine species ACRs would be 5.96. Potentially, the national nickel water quality criterion and Lower South San Francisco Bay site-specific criterion would be 24.42 and 20.94 μg/L, respectively.

On the other hand, if the marine and freshwater ACRs were combined, the resultant FACR would be 10.50. This could lead to the establishment of a national nickel water quality criterion and a San Francisco Bay site-specific criterion of 13.86 and 11.89  $\mu$ g/L, respectively.

This range of SSOs encompasses several scenarios (Recalculated National Criterion/Marine ACR; Recalculated National Criterion/Combined Freshwater and Marine ACR; South San Francisco Bay Site-Specific Objective/Marine ACR; and South San Francisco Bay Site-Specific Objective/Combined Freshwater and Marine ACR). These scenarios produced the potential SSO values for total nickel of 24.42, 13.86. 20.94, and 11.89 µg/L, respectively.

The chronic values of 22.09 and 26.43  $\mu$ g/L for mysids and abalone, respectively indicate that three of the four potential nickel SSOs would be protective (in clean laboratory water) of the more sensitive mysid. These are:

- Recalculated National Criterion/Combined Freshwater and Marine ACR (13.86 μg/L);
- South San Francisco Bay Site-Specific Objective/Marine ACR (20.94 μg/L); and
- South San Francisco Bay Site-Specific Objective/Combined Freshwater and Marine ACR (11.89 μg/L).

Either of these three potential nickel SSOs would be protective of the mysids and abalone and, as such, be protective of the Beneficial Uses of the Lower South San Francisco Bay. It should be noted, however, that these SSO values are based on clean laboratory toxicity test results and do not include any of the ambient "apparent complexing capacity" present in the Lower South San Francisco Bay that may be responsible for making nickel less bioavailable to aquatic organisms.

4.3.3.4 City of San Jose's Site-Specific Copper Study for Lower South San Francisco Bay

The City of San Jose (the City) (1998) used the Water Effects Ratio (WER) method of the **Indicator Species Procedure** to derive a site-specific WER and a site-specific water quality criterion that were based on dissolved copper. This, in accordance with the U.S. EPA (1995) recommendation that water quality criteria be based on dissolved, rather than total metals concentrations.

The City realized that the previous site-specific copper studies (Larry Walker Associates, et al. 1991a, b; S.R. Hansen & Associates, 1992a) were limited by the lack of both temporal and spatial data. This study was specifically designed to encompass a full year and provide enough sampling sites to be representative of the water quality of Lower South San Francisco Bay.

This study was limited to the extreme Lower South San Francisco Bay (South of Dumbarton Bridge). This area was chosen because Lower South San Francisco Bay has been designated by the State of California and the U.S. EPA as a water body that is adversely affected by toxic pollutants pursuant to Sections 304(l) and 303(d) of the Clean Water Act. The 1996 California 303(d) and TMDL Priority List designates the Lower South San Francisco Bay as impaired due

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to metals contamination with municipal point sources, urban runoff/storm sewer and surface mining listed as probable sources. In addition, the extreme Lower South San Francisco Bay is described in the 1995 Basin Plan as being unique:

"The South Bay below the Dumbarton Bridge is a unique, water-quality-limited, hydrodynamic and biological environment that merits continued special attention by the Regional Board. Site-specific water quality objectives [criteria] are absolutely necessary in this area for two reasons. First, its unique hydrodynamic environment dramatically affects the environmental fate of pollutants. Second, potentially costly non-point source pollution control measures must be implemented to attain any objectives for this area."

Additionally, the area south of the Dumbarton Bridge can be characterized as a "tidal lagoon" that is significantly influenced by POTW flow (Chen et al. 1996 and Cheng et al. 1993).

The study sites were selected to represent South San Francisco Bay and are described below:

- Dumbarton Bridge Sites Two sites were selected, one north and one south of the bridge. These were selected because they represented the boundary between the South Bay and the greater San Francisco Bay. They are also from the area that is least likely to be effected by POTW discharge and
- Coyote Creek Site This site was selected to represent the "shallow" nature of South San Francisco Bay and it was assumed to be more heavily influenced by POTW discharge, urban creek flow, and sediment scouring than the Dumbarton Bridge sites.

These three sites were selected because they were assumed and later verified to represent the two extremes of the South Bay with respect to site water binding capacity based on a previous study (S.R. Hansen & Associates 1992a). In addition, the choice of the two northernmost sites, expected to have the least amount of binding capacity, and only one southernmost station was employed as a conservative measure which could provide a margin of safety in the determination of a final site-specific criterion. A fourth site, 0.13 nautical miles north of the San Mateo Bridge was added later in the study to confirm an observed trend.

This study was initiated in January 1996 and completed in March 1997, with samples being collected every two weeks. This allowed the data set to represent a full annual hydrological cycle and would produce a more accurate estimate of the water quality characteristics present in Lower South San Francisco Bay.

The blue mussel (*Mytilus edulis*) was used since (1) it had an endpoint near, but above the national CCC of 4.9 µg/L (a requirement described in U.S. EPA 1994), (2) is the most sensitive species listed in the national marine criteria data set for copper (U.S. EPA 1985 and 1995), and (3) decisions based on its results would be protective of aquatic life. A secondary test using the purple urchin (*Strongylocentrotus purpuratus*) confirmed the WER values obtained with *M. edulis* within a factor of 1.27 and 1.35, respectively, for measured total and dissolved copper.

The results of this study (Table 4-10) revealed:

- WER values ranging from 3.5 to 5.1 and from 2.7 to 3.5 based on measured total and dissolved copper, respectively;
- Total and dissolved copper WER values increased from north to south and were statistically significantly greater at the southern station (near Coyote Creek and POTW flow) than at the two northernmost stations;
- The observed WERs based on total copper measurements were more variable for all stations (CV of 23-30%) than WERs based on dissolved copper measurements (CV of 14-20%), presumably due to the wide range of TSS for all stations over time (3.1 184 mg/L) and the significant positive correlations between total copper WERs, TSS, and wind velocity; and
- The WER results indicated that there was greater protection of aquatic life from copper toxicity at the southern end of the study area compared to the northern end due to particulate and dissolved binding capacity of the site water.

The lower variability in the dissolved copper WER results, when compared to the higher variability that was observed in total copper WER results, suggested that a Final WER (FWER) should be based on dissolved copper rather than on total copper measurements. Unlike total copper WERs, dissolved WERs were more consistent over time and were not influenced by the effects of changing wind velocities and TSS concentrations within the site. Further, the absence of seasonal, rainfall, or wind effects on the station-specific dissolved WER values supported the use of a single dissolved FWER value and subsequent site-specific water quality criterion across all seasons.

Table 4-10
Water Effects Ratio Values for Copper Obtained in Lower South San Francisco Bay

Site	Water Effects Ratios (CV%)	
	Total Copper	Dissolved Copper
Dumbarton North	3.497 (22.91)	2.670 (14.14)
Dumbarton South	3.830 (30.37)	2.876 (18.51)
Coyote Creek	5.056 (30.05)	3.535 (19.83)
2-Station Dumbarton Mean	3.660 (28.65)	2.771 (16.94)
3-Station Mean	4.076 (34.85)	3.005 (21.99)

From: City of San Jose (1998)

The national data-set was modified by incorporating this study's laboratory water toxicity data which resulted in the national CCC of 3.1  $\mu$ g/L (dissolved copper) being replaced by a new national CCC of 2.5  $\mu$ g/L (dissolved copper). Using this modified national criterion, site-specific CCC values were obtained for different locations within the South Bay site. These values ranged

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from 6.7 to 8.8  $\mu$ g/L as dissolved copper. The City (1998) stated that, "in awareness of the regulatory difficulties associated with a multi-criteria approach, the most appropriate site-specific Criterion Continuous Concentration (CCC) for the South Bay is 6.9  $\mu$ g/L as dissolved copper". This value was based on pooled WER results from the two Dumbarton Bridge stations. The proposed site-specific criterion of 6.9  $\mu$  g/L (dissolved copper) would be protective of *M. edulis*, the most sensitive species listed in the national marine criteria data set for copper.

The authors suggest that the two-station site-specific criterion of  $6.9 \,\mu\text{g/L}$  (dissolved copper), while being overprotective of areas to the south, is the most appropriate site-specific copper criterion and meets the requirements of being conservative, protective, and appropriately derived. Further, the WER values derived in this study indicate that the previously established WER of  $1.7 \, \text{appears}$  to be overly protective of the Lower South San Francisco Bay environment.

Dr. Glen Thursby (U.S. EPA, Narragansett, RI) reviewed this study for the City of San Jose and indicated that the City took the conservative approach in almost every decision that they made. However, he suggested that the data do indicate that a second WER value may be appropriate for the "sub-area" represented by the Coyote Creek station. This is provided that the Coyote Creek WER value is representative of the entire sub-area. In addition, he stated that a WER that was based solely on the two northern-most stations may be "too overly protective" for the Coyote Creek sub-area.

### 4.3.3.5 Site-Specific Case Studies Summary Conclusions

The Site-specific case studies for San Francisco Bay and Lower South San Francisco Bay have demonstrated, rather conclusively, that:

- The toxicity of copper and nickel is less in ambient site-water than the national water quality criteria predict (e.g., WER values significantly different from 1);
- The amount of bioavailable copper and nickel is reduced by the presence of components that make up the apparent complexing capacity of Lower South San Francisco Bay. These components can bind with the copper and nickel, making copper and nickel biologically unavailable (e.g., natural or anthropogenic organic ligands) or compete for receptor sites on, or in, the organism (e.g., manganese and iron);
- This apparent complexing capacity is greatest in the extreme northern and southern portions of San Francisco Bay;
- The amount of bioavailable copper decreases in the Lower South San Francisco Bay on a north to south basis;
- The national criteria for copper and nickel are over-protective of the beneficial uses of Lower South San Francisco Bay; and

• The Lower South San Francisco Bay may require multiple WER values (i.e., one for the northern most and one for the southern most reaches).

Each of the previously described studies had limitations in the quality of the data that could affect the accuracy and appropriateness of the site-specific criteria that were proposed. These ranged from a lack of temporal and spatial data to a lack of a large saltwater ACR database. The quality of the available data for each of these studies is discussed in the following section.

### 4.3.3.6 Quality of Available Data

The toxicity bioassay data that have been used to re-calculate national criteria for copper and nickel underwent extensive quality control/quality assurance protocols; beginning with,

- The initiation of the individual toxicity bioassay tests (which are performed under rigorous quality control criteria as described in the appropriate EPA testing protocols), and followed by
- The final data values being subjected to a rigorous peer review that compares them to the minimum quality control criteria that are required for usage in calculating the national water quality criteria (Stephan et al. 1985).

If the data meet the minimum requirements for acceptance, they are then used to calculate a criterion (national or site-specific); if they are found to be deficient, they are rejected.

In addition to quality, we must look at quantity and appropriateness of data. Too few data points, as well as broad generalizations (e.g., all segments of the Bay behave similarly) provide a much "coarser" estimate of actual ambient conditions. With this in mind, we look at each of the abovementioned site-specific studies.

### Cities of San Jose/Sunnyvale E5E NPDES Studies (Copper and Nickel)

**Temporal limitations** - This study was limited in that sampling occurred only during the "wet" season (February to June) and, as a result, the data are incomplete and may not be representative of water quality conditions in Lower South San Francisco Bay during the entire year.

### San Francisco Regional Water Quality Control Board Copper Site-Specific Study

**Temporal limitations** - This study was limited in that sampling occurred only during the "dry" season (May to October) and, as a result, the data are incomplete and may not be representative of water quality conditions in Lower South San Francisco Bay during the entire year.

**Spatial limitations** - Six stations were selected for use in this study (only two of which were located in Lower South San Francisco Bay).

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**Test species limitations -** This study selected two sensitive test species to develop a site-specific copper criterion (oyster, *C. gigas* and diatom, *T. pseudonana*). While both of these species are sensitive to copper, the mussel *M. edulis* is more sensitive than *C. gigas*. *C. gigas* was used as a surrogate for *M. edulis* in this study because *M. edulis* was not in spawning condition during the study period. The diatom test results were not used to determine a water quality objective because of the sample manipulations required to test the algae (filtration and nutrient addition) and the ability of some phytoplankton species to produce phyto-chelators that reduce metal toxicity that makes data interpretation difficult. Thus, a water quality objective was set using only one test species which is less than optimal (Gary Chapman, 1992. U.S. EPA review comment on study).

**Algal metal exposure measurements -** This study reported measured total and dissolved copper concentrations in algal test solutions prior to test initiation but not at the conclusion of the tests. Thus, only the initial exposure and nothing about the overall exposure is known. Since algae have the ability to produce phyto-chelators, the actual exposure concentration remains unknown.

Algal test anomalies – Two of the South Bay *T. pseudonana* test data were not included in this impairment assessment analysis because the concurrent reference toxicant tests indicated that the test organisms were overly sensitive to copper during one test event and overly resistant to copper on another test date. The data indicated that on those two occasions, the control water (ambient Bodega Bay seawater) may have contained toxicants other than copper (causing the more sensitive test response) or elevated complexing capacity (causing the more resistant toxicity response). These anomalies cast suspicion over the validity of those test results.

### San Francisco Regional Water Quality Control Board Nickel Site-Specific Study

This study was preliminary and included only one sample date for each of two species (oyster, *C. gigas* and urchin, *L. pyctus*). The data indicate that the white urchin, *L. pyctus* was most sensitive to nickel, but nothing conclusive can be, or was, presented.

### City of San Jose Nickel Recalculation & Site-Specific Criterion Study

**Limited number of saltwater ACRs** - Only 4 saltwater and 2 freshwater ACR are available. This means that the recommended Final Chronic Value will be derived using a combination of both freshwater and saltwater organisms.

The sensitivity results of additional resident saltwater organisms from different families needs to be tested and added to the test data-set before a completely saltwater ACR can be calculated; however the recalculation and subsequent development of a site-specific criterion for nickel provided by Watson, et al. (1996; 1999) provide adequate and updated information for development of a site-specific criterion and a national criterion for nickel when the combined freshwater and saltwater ACR value is used.

### City of San Jose Site-Specific Study for Copper

**Spatial limitations** - This study selected only three sites within South San Francisco Bay (One near Coyote Creek to the south and two near Dumbarton Bridge to the north) due to limited resources. Additional sites in the "central" portion of South Bay would have provided more information on the water quality of the main water mass in South Bay (to compensate for this, the City used the more conservative WER values obtained from the Dumbarton Bridge sites to develop the copper site-specific criterion).

The quality and quantity of the data obtained by the City of San Jose during their development of a site-specific criterion for copper are the most comprehensive of all of the studies. This study used the most sensitive indicator species (*M. edulis*, which is currently available in spawning condition all year) and sampled over the course of a full year.

A review of the data and conclusions was provided by Dr.Glen Thursby (U.S. EPA, Narragansett, RI). Dr. Thursby stated that, "When the authors had to make decisions on how to apply the data, for the most part they chose to be environmentally conservative;" Dr. Thursby added, "The data are valid and as good as any I have seen for toxicity tests. Given the time span covered and the number of toxicity tests run, there is a remarkable 'tightness' to the data;" and concluded with, "The conclusions are reasonable given the results obtained. The authors built in a lot of conservatism within the various steps along the way (e.g., initial dissolved copper values only, adjusting for the effect of adding salts, omitting Coyote Creek WERs from the final WER, and using a cmcWER for the CCC." Dr. Thursby also mentioned that maybe a WER value of 2.8 was overprotective of the southern reaches of the South Bay and that possibly a second, higher WER for that area might be appropriate.

### 4.3.4 Can this Indicator be used in South San Francisco Bay?

The sensitivities of resident aquatic organisms to copper and nickel in ambient site water has been utilized as an indicator of impairment of beneficial uses in San Francisco Bay (Larry Walker Associates, et al.,1991a, b; SRH&A, 1992; and City of San Jose, 1998); with the 1992 study playing a major role in setting the previous site-specific water quality objectives for copper. The California Regional Water Quality Control Board: San Francisco Bay Region (Basin Plan) (1995) currently use the results obtained from these site-specific studies as guidance in setting discharge permit limits in San Francisco Bay. The City of San Jose site-specific study (1998) confirms the fact that the national criterion are overprotective for the Lower South San Francisco Bay and refines the database by being specific to Lower South San Francisco Bay.

Water Quality Attainment - This indicator could be applied to Lower South San Francisco Bay by determining a site-specific WER and multiplying the WER against the national aquatic water quality criterion for copper or nickel. The product of this would become the site-specific criterion for either copper or nickel for the Lower South San Francisco Bay. Ambient levels of copper and nickel in Lower South San Francisco Bay would be compared to these criteria. Ambient concentrations above the criteria are assumed to pose potential threats to beneficial uses.

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Copper – Figure 4-6 compares the ambient total copper concentrations observed in the Lower South San Francisco Bay between 1989 and to the "current" water quality objective for San Francisco Bay of 4.9  $\mu$ g/L (total copper). These data (n = 784) indicate that total copper concentrations in Lower South San Francisco Bay have been frequently above the water quality objective, and appear to be cyclic; with a greater number of elevated values occurring during the dry season (May – October). This may be caused by the increased wind action during the summer months which churns the sediment bed, increasing the concentration of suspended solids in the water column and results in the sediment-bound copper being included as a "water-column copper" measure. This supports the claim by the City of San Jose that total copper in the water column is directly affected by winds and suspended solids and that a water quality objective for copper in the Lower South San Francisco Bay that is based on dissolved concentrations of copper would be more appropriate.

The dissolved copper concentrations observed in Lower South San Francisco Bay between 1989 and 1999 are presented in Figure 4-7. These data are compared to the national water quality criterion (proposed CTR) value of 3.1 µg/L (dissolved copper). These data indicate that during this ten-year period, dissolved copper concentrations were frequently above the proposed criterion value. In addition, the high values follow the same seasonal pattern that was observed with the total copper concentrations in the Lower South San Francisco Bay, with a greater number of the elevated concentrations occurring during the dry season. When comparing the data on Figure 4-7 to the national criterion, it must be remembered that the national criterion was calculated using toxicity test results obtained from laboratory waters. These tests should be considered to be "worst-case" as described in the U.S. EPA Guidance (Stephan, et al. 1985). Some metals, especially copper, form reduced-toxicity complexes with dissolved organic compounds and colloids. These reduced-toxicity complexes would not be distinguishable from the bioavailable fraction of copper in a "dissolved" sample. This means that ambient dissolved copper values that are above the national dissolved copper water quality criterion may not result in a toxic response by aquatic organisms. A much better application of the dissolved copper water quality criterion is to calculate a site-specific criterion that, by definition, takes into consideration the amount of bioavailable copper on a site-specific basis. The site-specific criterion for copper of 6.9 µg/L (dissolved) for Lower South San Francisco Bay that was proposed by the City of San Jose (1998) is compared to the ambient dissolved copper concentrations that have been observed in the Lower South San Francisco Bay (Figure 4-7). The ambient Lower South San Francisco Bay site-specific water quality criterion value of 6.9 µg/L dissolved copper provided by the City of San Jose (1998) is based on the response of aquatic organisms to site-water and indicates that the current national water quality criterion for copper (3.1 µg/L dissolved) is overprotective of the Beneficial Uses of the Lower South San Francisco Bay. Ambient concentrations of dissolved copper in the Lower South San Francisco Bay have been below the proposed site-specific water quality criterion of 6.9 µg/L for dissolved copper since mid-1990 (Figure 4-7). Thus indicating that current ambient concentrations of dissolved copper in the Lower South San Francisco Bay are below the threshold concentration of dissolved copper above which impairment of the Beneficial Uses could potentially occur (i.e., proposed SSO).

Nickel - Comparisons of ambient Lower South San Francisco Bay dissolved nickel concentrations to the National water quality criterion and local water quality objective, and proposed site-specific water quality objectives for nickel (Watson, et al. 1996, 1999) are summarized in Figure 4-8. This figure is a graphical representation of data collected between 1989 and 1999 with comparisons made to the above mentioned criterion, objective, and proposed criteria. Since the proposed nickel criteria and site-specific objectives are based on "total" nickel, a conversion factor of 0.98 is used to convert the proposed criteria to "dissolved" (Dan Watson, personal communication, 1999). This conversion factor represents the percentage of the total measured nickel in the test solutions that was in the dissolved phase. The ambient Lower South San Francisco Bay dissolved nickel concentrations were sporadically above the National saltwater criterion and the San Francisco Bay water quality objective of 8.1 µg/L (dissolved) (13 out of 245 samples, or 5 percent) during this ten year period. Ambient dissolved nickel concentrations were greater than the proposed dissolved SSO of 11.7 µg/L (combined freshwater and marine ACRs) once during this same time period (1 out of 245 samples, or 0.4 percent). Ambient dissolved nickel concentrations in the Lower South San Francisco Bay during the same time period were never greater than the proposed dissolved SSO of 20.5 µg/L (using the marine ACR, as proposed by Watson, et al. 1999).

### 4.3.5 Combined AERAP and Site-Specific Indicator Impairment Analysis

This analysis combines the AERAP (section 4.2) and Site-Specific Indicators to evaluate the potential for Beneficial Use impairment due to ambient concentrations of dissolved copper in Lower South San Francisco Bay.

Comparison of WER adjusted 95% ERC with expected environmental concentrations (EECs)

The range of ambient or expected environmental concentrations (EECs) for dissolved copper at twenty nine different water quality monitoring stations in Lower South San Francisco Bay for both wet and dry seasons (n = 58) is compared to the cumulative frequency curve of the AERAP where the toxicity database has been WER adjusted. The toxicity sensitivity values for the resident/surrogate toxicity database were multiplied by the WER value of 2.77. This adjustment accounts for the apparent complexing capacity of Lower South San Francisco Bay waters as determined by the City of San Jose Site-Specific Study (1998). The 95% ERC for this WER adjusted AERAP calculation is 8.6µg/L dissolved copper.

The purpose of this component of the analysis is to provide stakeholders with a better understanding of the relationship between the WER adjusted 95% ERC for resident and surrogate species with ambient concentrations of dissolved copper. The water quality data from the 29 Lower South San Francisco Bay monitoring stations that are used in the comparisons, is summarized in Table 4-11a,b. The stations with the highest and lowest mean values are used for the comparisons. These comparisons are illustrated in Figures 4-9 and 4-10. Station C-3-0 Dry Season has the highest mean concentration of dissolved copper (5.4  $\mu$ g/L). Station SB-12 Wet Season has the lowest mean concentration of dissolved copper (1.5  $\mu$ g/L). These stations also have the highest concentration measured (5.9 $\mu$ g/L) and the lowest concentration measured (0.9 $\mu$ g/L), thus bracketing conditions for the period of record in South San Francisco Bay. The

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maximum ambient dissolved copper concentration value or EEC does not approach the lowest toxicity value for the most sensitive species in the WER adjusted toxicity database, indicating that Beneficial Uses were not impacted during the time period 1989 to 1999. For the locations of the stations included in this analysis, refer to Figure 4-4.

Without accounting for any apparent binding capacity at the monitoring stations the plots suggest that ambient concentrations could periodically result in chronic effects to some of the most sensitive species in Lower South San Francisco Bay. The plots also suggest that for the vast majority of cases ambient concentrations of dissolved copper are well below the effects level of the most sensitive species in the resident species toxicity database.

### Hypothesis Testing

A series of hypothesis tests were conducted to more rigorously compare ambient concentrations (EEC) to the 95% WER adjusted ERC. The AERAP uses a one-tailed, two-sample t-test for testing the probability that the mean EEC is greater than the distribution of the ERC. The  $\alpha$  for the hypothesis test is .05. The null hypothesis for the test:

O: Mean EEC = Mean ERC

A: Mean EEC > Mean ERC

The results of the hypothesis tests are listed in Table 4-11a,b. The null hypothesis was not rejected at any of the stations for either the wet or dry seasons. These hypothesis tests results indicate that the mean of the ambient (EEC) concentration distributions for dissolved copper did not exceed the 95% WER adjusted ERC value of  $8.6\mu g/L$  during the time period 1989 to 1999. The ERC is the concentration of dissolved copper that is estimated to protect 95% of community taxa.

#### 4.3.6 Uncertainties

The consequences of the decisions that are made regarding the setting of site-specific objectives extend well into the future. For this reason, it is essential that predictions of the effects of allowable concentrations of copper and nickel in Lower South San Francisco Bay be technically sound and based on the best available scientific information. However, the presence of uncertainty complicates the ability to make absolute statements and thus, technically based estimates can only be made. In addition, decision-makers need to be provided a measure of the magnitude of the uncertainty associated with decision criteria to then be able to effectively weigh and use the results of these environmental analyses. These issues are addressed in the impairment assessment by making a vigorous effort to identify the magnitude and sources of uncertainty associated with each of the indicators that are used in the impairment assessment and that are used in the development of alternatives for site-specific objectives.

Uncertainty is defined herein as the state or condition of incomplete or unreliable knowledge. For each indicator evaluated or analysis conducted in this assessment, both the sources and the magnitude of known uncertainties are identified. The sources include natural variability, sample

variability, and the appropriateness of models that are used in making predictions. Where possible, the magnitudes of identified uncertainties are addressed using descriptive statistics and by setting confidence limits on predicted values. In the absence of quantitative information, a professional judgement of the value of the existing information is presented.

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Table 4-11a

The Expected Environmental Concentrations (μg/L) for Dissolved Copper during the Wet Season at the Water Quality Monitoring Stations used in the AERAP Analysis

Station ID	N =	Minimum	Mean	Maximum	SD	t-Stat	p-Val
SBDA							
	_						
C-1-3	7	2.6	3.1	3.8	0.5	-16.6	1.0
C-3-0	7	2.6	3.4	4.3	0.6	-14.4	1.0
C-5-0	6	3.0	3.5	3.9	0.4	-14.7	1.0
C-6-0	6	3.2	3.5	4.3	0.4	-14.7	1.0
R-4	7	2.8	3.5	4.5	0.6	-14.0	1.0
SB-4	6	1.4	3.0	4.0	0.9	-7.5	1.0
SB-5	7	2.6	3.2	4.1	0.5	-16.2	1.0
SB-6	6	2.4	3.3	4.0	0.5	-15.0	1.0
SB-7	7	2.7	3.3	3.8	0.4	-15.5	1.0
RMP							
BA-10	7	1.6	3.3	4.9	1.2	-6.2	1.0
BA-20	8	1.8	2.9	5.0	1.0	-8.0	1.0
BA-30	8	1.9	2.7	3.7	0.6	-12.4	1.0
C-1-3	7	1.4	2.5	4.8	1.3	-6.3	1.0
C-3-0	7	1.6	3.4	5.9	1.4	-5.4	1.0
San Jose WER							
DBN	12	1.4	2.2	3.3	0.4	-21.3	1.0
DBS	12	1.7	2.5	3.5	0.5	-17.6	1.0
CC	12	2.0	2.7	4.1	0.7	-13.1	1.0
South Bay							
SB01	19	1.4	1.9	2.4	0.3	-33.7	1.0
SB02	18	1.5	2.0	3.4	0.5	-33. <i>1</i> -21.1	1.0
SB03	18	1.3	2.0	3.4	0.5	-21.1 -21.1	1.0
SB04	18	1.6	2.2 2.5	3.2 3.2	0.5	-21.1 -20.9	1.0
SB05	18	1.5	2.3	3.2 3.6	0.5	-20.9 -18.2	1.0
SB06	17	1.5	2.3	3.2	0.6	-10.2	1.0
SB07	17	1.5	2.1	3.4	0.5	-20.6	1.0
SB08	19	1.5	2.2	3.1	0.3	-25.7	1.0
SB09	19	1.5	2.2	3.1	0.4	-25.7	1.0
SB10	20	1.6	2.4	3.9	0.4	-19.0	1.0
SB11	13	1.2	1.9	3.2	0.6	-15.6	1.0
SB12	15	0.9	1.5	2.5	0.4	-22.5	1.0

95% Confidence Level (Reject H0) The null hypothesis was accepted at all stations for wet seasons.

Table 4-11b

The Expected Environmental Concentrations (µg/L) for Dissolved Copper during the Dry Season at the Water Quality Monitoring Stations used in the AERAP Analysis

Station ID	N =	Minimum	Mean	Maximum	SD	t-Stat	p-Val
CDD 4							
SBDA							
C-1-3	7	3.1	5.3	8.9	2.1	-2.6	1.0
C-3-0	7	3.3	5.4	9.4	2.2	-2.4	1.0
C-5-0	6	3.6	4.9	7.3	1.7	-3.1	1.0
C-6-0	6	3.0	4.8	7.9	1.9	-3.0	1.0
R-4	7	2.6	4.6	6.8	1.6	-3.9	1.0
SB-4	6	2.6	3.8	6.3	1.3	-5.0	1.0
SB-5	7	2.2	4.0	6.5	1.5	-4.7	1.0
SB-6	6	2.2	4.5	7.0	1.7	-3.5	1.0
SB-7	7	2.3	4.4	6.6	1.5	-4.3	1.0
RMP							
BA-10	5	3.1	3.6	4.5	0.6	-12.2	1.0
BA-20	7	2.5	3.3	4.4	0.6	-14.8	1.0
BA-30	7	2.4	3.0	3.7	0.5	-17.1	1.0
C-1-3	5	2.0	3.2	4.3	0.9	-6.7	1.0
C-3-0	5	2.1	3.3	4.1	0.9	-6.7	1.0
000	Ü	2.1	0.0		0.0	0.7	1.0
San Jose WER							
DBN	13	2.1	2.8	3.7	0.4	-23.2	1.0
DBS	13	2.3	2.9	3.7	0.4	-22.7	1.0
CC	13	2.5	3.4	3.9	0.4	-19.9	1.0
South Bay							
SB01	22	2.6	3.0	3.6	0.3	-28.9	1.0
SB02	20	2.3	3.1	4.2	0.5	-21.3	1.0
SB03	20	2.6	3.3	4.1	0.4	-23.0	1.0
SB04	19	1.7	3.0	4.3	0.9	-12.9	1.0
SB05	21	1.6	3.2	3.9	0.6	-17.9	1.0
SB06	21	2.6	3.4	4.3	0.5	-20.2	1.0
SB07	22	1.8	3.3	4.2	0.6	-18.0	1.0
SB08	22	2.9	3.4	4.4	0.4	-23.0	1.0
SB09	22	2.4	3.3	4.2	0.4	-23.6	1.0
SB10	22	2.9	3.6	4.6	0.4	-21.8	1.0
SB11	14	1.0	1.9	3.4	0.7	-14.2	1.0
SB12	13	0.9	1.7	4.4	0.9	-11.2	1.0

95% Confidence Level (Reject H0) The null hypothesis was accepted at all stations for dry seasons.

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The uncertainties and issues that are associated with this indicator are listed below:

Uncertainty - The assumption that the response of a test organism to a given stressor or stressors (when exposed at a sensitive life stage) mirrors the response that the test organism would exhibit if exposed to the stressor for its entire life provides a certain level of uncertainty. Ideally, aquatic toxicity bioassay tests would expose the test organism to a stressor for the duration of its life-cycle (cradle-to-grave). In actuality, only the easiest "most sensitive life stage" (generally, an early life stage) is what gets tested (due to the logistics and cost of full life-cycle tests). The exposure may be either short-term (acute - from a few minutes to 4-days) or longer-term (chronic - one week to 90 days).

Resolving this Uncertainty - The early life-stage of most organisms is when they're most sensitive to toxicants (e.g., copper and nickel). For this reason, the use of early life-stages is a general requirement of most toxicity testing protocols (U.S. EPA 1991). Therefore, if the exposure to a toxicant occurs during the early life-stage (i.e., the most sensitive life-stage) the resultant toxicological value (and subsequent water quality criterion) would be protective of that organism and, as such, partial life-cycle tests which use early life-stage organisms provide an adequate measure of protection.

**Recommended Action -** None. All tests used early life-stage organisms.

Uncertainty - Direct projection of toxicity test results obtained under very controlled laboratory conditions to predict ambient toxicity responses limit the accuracy and add uncertainty to any analysis. Several conditions (e.g., toxicant exposure, temperature, photoperiod (light intensity and duration), and presence or absence of predatory stress) have the potential to be much different between the laboratory and ambient site (Diamond et al. 1999 et al. and citations therein).

**Resolving this Uncertainty -** This uncertainty can be reduced by adequately characterizing the ambient conditions prior to testing. Many of the ambient conditions can be duplicated, to some extent, in the laboratory (e.g., photo-period and intensity can be duplicated by using appropriate lighting and timers/dimmers; ambient temperature can be duplicated by using thermo-controllers; and salinity can be maintained using natural or artificial salts). These will only serve to reduce the uncertainties since the effects of environmental fluctuations (e.g., cloud cover, freshwater runoff/rain, and predators) cannot be easily duplicated.

**Recommended Action -** None. All toxicity tests used standardized bioassay protocols that include controlling environmental factors to the greatest extent possible.

**Uncertainty -** The uncertainty based on the assumption that using surrogate test species provides an adequate estimate of the sensitivity of native species to a

particular toxicant depends on the quality of the surrogate test organisms. Laboratory culturing of these surrogates imparts uncertainty to tests regardless of whether the species is fundamentally appropriate to use as surrogates. Nutritional and behavioral requirements of these surrogate species are not fully understood, which may lead to variable results in toxicity testing that have no actual relationship to indigenous biota. Many of the species that are used in these toxicity tests are non-resident and, therefore, surrogate test species (closest genus match) are used.

Resolving this Uncertainty - There is a certain amount of controversy regarding the appropriateness of using test surrogates. Stephan et al. (1985) states that, "On the average, species within a genus are toxicologically much more similar than species in different genera." He also states that applying the appropriate surrogate will provide an adequate amount of protection for resident species. The level of uncertainty associated with surrogates can be reduced by adequately characterizing the culturing requirements of a proposed surrogate test species prior to its use. In addition, it is imperative that careful attention be paid to the health of the culture stock health.

**Recommended Action -** Generate a "resident species" data-set. In the interim, use only surrogate species that appropriately represent the resident species population. This means using surrogates that are as closely related to residents as possible (i.e., same genera) and were obtained from reputable culturing facilities.

Uncertainty - There is a level of uncertainty associated with the organisms that comprise the national data-set. This uncertainty arises with the possibility that there are resident organisms that are more sensitive to copper and nickel than those in the data-set that either cannot or have not been tested due to difficulties in collection, culturing, and testing. The paucity of data on phytoplankton assemblages (cyanobacteria, coccolithophores and dinoflagellates) that have been reported to be more sensitive to copper than the species that are included in the national database could, if quality information is not available, cause these organisms to be non-protected. The existence of species that are more sensitive to copper than those included in the national data-set present a level of uncertainty as to whether there are other species (perhaps more ecologically relevant) which are more sensitive to copper and are not being protected.

Resolving this Uncertainty - Plants and algae species are not generally used to set water quality criteria because of the difficulty in interpreting the results. However, plants and algae should be protected (if they are ecologically important) (Mount 1992). The lack of adequate toxicological data on these sensitive phytoplankton assemblages could be remedied by performing standardized toxicity tests using them. This would add to the national data-set and, if necessary, allow for the re-calculation of a criterion that would be protective of them. On the whole, the U.S. EPA (1984) states that a criterion that is protective of the most sensitive aquatic animal should also be protective of phytoplankton.

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Identification of sensitive resident species and determination of the toxicology of copper and nickel would be the first steps in addressing the potential for ecologically important species that currently remain unknown and, possibly unprotected.

**Recommended Action -** Fully characterize the components of the ambient water. Knowledge of what comprises any observed apparent complexing capacity will allow for a more complete understanding of how metals bioavailability can be influenced by filtration and added nutrients. In addition, resident phytoplankton species need to be isolated and their sensitivities to copper and nickel determined in both laboratory and ambient waters.

Temporal and spatial water quality variability pose uncertainty for site-specific studies that do not collect an adequate amount of data. If the data-set is not complete, short-term and local effects may be missed and cause the characterization to be less accurate. This occurred during the Larry Walker Associates et al (1991a, b) and S.R. Hansen & Associates (1992a, b) studies. These studies were both limited temporally by collecting only during either the wet or dry seasons. In addition, the S.R. Hansen & Associates (1992a, b) study did not contain enough sample stations in the Lower South San Francisco Bay and therefore, not enough data points were collected to adequately characterize that body of water.

**Resolving this Uncertainty -** This uncertainty is the easiest to remedy. Studies that wish to develop site-specific water quality criteria must include data that are temporally and spatially sound. Only an adequate number of data will provide an accurate estimate of the variability in water quality characteristics and result in an appropriate site-specific water quality criterion being derived.

**Recommended Action -** Use data-sets that contain as much temporal data as possible. The City of San Jose Site-Specific WER study includes data that matches this description, therefore, this is the data-set that is recommended by the assessment team.

**Uncertainty -** A limited number of saltwater ACRs for nickel limited the Watson, et al. (1996; 1999) recalculation studies. As a result, uncertainty was introduced into the proposed site-specific criterion when freshwater ACRs had to be included in the calculation of a site-specific criterion for nickel.

**Resolving this Uncertainty -** Additional acute and chronic testing of resident and non-resident saltwater species in laboratory water and including the results in the national data-set will allow for saltwater ACRs to be calculated that are based entirely on the response of saltwater organisms. This will ultimately provide a saltwater ACR that is fully protective of beneficial uses, while not being overly protective.

**Recommended Action -** Complete the data-set with both acute and chronic data using resident species, if possible, and appropriate surrogates if necessary. This will allow an ACR to be calculated that is based entirely on marine organisms and subsequently, site-specific water quality objectives that are fully protective of the beneficial uses of Lower South San Francisco Bay without being overly protective.

#### 4.3.7 Conclusions

This indicator provides a more accurate estimate of the sensitivities of aquatic life to copper and nickel in ambient Lower South San Francisco Bay site waters. It has repeatedly demonstrated that:

- The toxicity of copper and nickel is less in ambient site-water than the national water quality criteria predict (e.g., WER values significantly different from 1);
- The amount of bioavailable copper and nickel is reduced by the presence of components that make up the apparent complexing capacity of Lower South San Francisco Bay. These components bind with the copper and nickel, making copper and nickel biologically unavailable (e.g., natural or anthropogenic organic ligands) or compete for receptor sites on, or in, the organism (e.g., manganese and iron);
- This apparent complexing capacity is greatest in the extreme northern and southern portions of San Francisco Bay;
- The amount of bioavailable copper decreases in the Lower South San Francisco Bay on a north to south basis;
- The national criteria for copper and nickel are over-protective if ambient site-water tests are used as the main indicator of beneficial use impairment in Lower South San Francisco Bay; and
- The Lower South San Francisco Bay may require multiple WER values (i.e., one for the northern most and one for the southern most reaches).

### 4.4 Phytoplankton

The use of phytoplankton as an indicator of beneficial-use impairment in Lower South San Francisco Bay is appealing for several reasons. Phytoplankton are an essential part of the food chain that supports all ecological beneficial uses of the Lower South Bay. Phytoplankton also play an essential role in the biogeochemical cycling of copper and nickel. Additionally, there is a substantial body of scientific evidence that shows very low concentrations of free ionic copper in marine and estuarine systems can be toxic to phytoplankton. This last point has been a primary issue identified by TMDL Work Group members. There is a concern that the absence of cyanobacteria, coccolithophore, and dinoflagellate species in the Lower South Bay may be the result of copper toxicity.

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This section of the report first provides background information on the importance of phytoplankton in the Lower South Bay ecosystem. The role of phytoplankton in biogeochemical cycling and the behavior of copper and nickel in the aquatic environment are reviewed. An emphasis is placed on identifying the chemical forms of these metals that are potentially toxic to phytoplankton and potential uptake pathways. The concentration of these chemical forms of copper and nickel in the Lower South Bay are also bracketed. Much of this background information is summarized from a companion TMDL document – *Task 1 Conceptual Model Report for Copper and Nickel in Lower South San Francisco Bay* (Tetra Tech, 1999).

An extensive review of the literature on phytoplankton toxicity was conducted as part of the impairment assessment. A concerted effort was made to relate the findings of the most recent scientific investigations to the measured or estimated concentrations of copper and nickel that occur in the Lower South Bay. Information on the composition of the phytoplankton community in the Lower South Bay was also compiled. In the final part of this section, the information presented on copper and nickel toxicity is evaluated with an emphasis on determining the relevancy of using existing phytoplankton information as a basis for judging whether or not the beneficial uses of Lower South San Francisco Bay are impaired.

# 4.4.1 Biogeochemical Cycling of Copper and Nickel in the Lower South San Francisco Bay and Our Understanding of Copper and Nickel Effects on Phytoplankton

## 4.4.1.1 Phytoplankton Effects on Biogeochemical Cycling in the Lower South San Francisco Bay

The most important biological component of the biogeochemical cycles of copper and nickel in South San Francisco Bay is processing by the phytoplankton community. Phytoplankton are well known to control nutrient cycles in water, and could therefore be expected to have a significant effect on the cycling of nutrient metals. Phytoplankton remove dissolved copper and nickel from the water column through uptake processes. The removed metals are incorporated into algal cells, which settle to the sediments or are assimilated by algal and detrital consumers. The net effect is a reduction in dissolved water column concentrations of the metals, and an increase in organic particulate forms of the metals, most of which accumulate in the sediments before being regenerated and released. Phytoplankton uptake and regeneration play an important role in copper and nickel cycling in the oceans, and are thought to control the vertical concentration profiles of these metals in the upper portion of the water column (Bruland et al., 1991; Sunda and Huntsman, 1995). However, the importance of phytoplankton uptake in estuaries is less clear. Dissolved copper depletion during phytoplankton blooms has not been demonstrated in either South San Francisco Bay (Luoma et al., 1998) or in other estuaries (Slauenwhite et al., 1991). However, significant nickel removal, as well as reduction of other metals such as zinc and cadmium, was detected during a bloom in South San Francisco Bay (Luoma et al., 1998). This suggests that phytoplankton uptake of metals could be an important process. Lack of copper depletion could be due to other processes (e.g., significant copper sources) that exceed the magnitude of the phytoplankton uptake.

In order to assess the importance of biological cycling, phytoplankton uptake removal fluxes were estimated for copper and nickel in the Conceptual Model Report (Tetra Tech, 1999). These

fluxes were then compared to the loads and other major physical and chemical fluxes to determine their relative significance. Uptake fluxes were calculated using the product of measured phytoplankton growth fluxes and estimates of the metal concentrations in phytoplankton cells. Since copper and nickel concentrations have not been directly measured in San Francisco Bay phytoplankton, they were estimated from other sources in the literature that expressed phytoplankton uptake rates and cell metal concentrations in terms of free ion concentrations. This allowed the results to be extrapolated to South San Francisco Bay, since the copper and nickel speciation had previously been characterized by Donat et al. (1994).

The average phytoplankton uptake fluxes estimated in the Conceptual Model Report (Tetra Tech, 1999) were about the same order of magnitude as the POTW loads of copper and nickel to the Lower South San Francisco Bay. Phytoplankton uptake fluxes were greater than the estimated sediment diffusion fluxes and atmospheric loads, but they were much less than sediment resuspension and tributary runoff loads. In addition to their effect on metal removal from the water, phytoplankton blooms can affect copper speciation and bioavailability through the release of organic compounds during blooms and bloom senescence (Sanders and Riedel, 1993). Also, some of the copper and nickel removed during phytoplankton uptake is recycled back to the water column through decomposition and mineralization of settled phytoplankton in the sediments.

### 4.4.1.2 Conceptual Model of Phytoplankton Uptake and Toxicity

The important processes involved in the uptake and toxicity of copper and nickel in phytoplankton were presented in the Conceptual Model Report (Tetra Tech, 1999) and are described below. Figure 4-11 summarizes the processes for copper. The same general concepts also apply to nickel. However, nickel has been much less studied than copper, so less information is available on nickel uptake and toxicity in phytoplankton.

Copper, nickel, and other metal ions are transported into phytoplankton cells by transport proteins on the cell membrane. These proteins carry the metals across the cell membranes and release them into the cytoplasm. The receptor sites on the transport proteins compete with binding sites on suspended particles (adsorption) and organic and inorganic ligands for free metal ions. Uptake and toxicity depend on the concentration of either the free metal ion or the sum of the free ion and labile inorganic complexes. In this report, we refer to these forms as the bioavailable forms of the metals. Metals complexed to strong organic ligands or adsorbed to suspended particles are not available for uptake since they cannot cross the cell membrane. However, these metals are still ultimately available to the system since complexation/dissociation reactions and adsorption/desorption reactions continually exchange free ions with the solution.

In South San Francisco Bay, 8 to 20 percent of the dissolved copper and 50 to 66 percent of the dissolved nickel occurs as inorganic (and weak organic) complexes and free metal ions (Donat et al., 1994). The rest of the dissolved copper and nickel are complexed with strong organic ligands. Two classes of ligands have been identified for the metals, one representing very strong complexes, and another representing moderately strong complexes (Donat et al., 1994; Sedlak et al., 1997). The majority of dissolved copper in South San Francisco Bay is bound to the weaker of the two ligands that complex with copper, while almost all of the complexed nickel is

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associated with the strong ligand that complexes with nickel (Donat et al., 1994; Bedsworth and Sedlak, 1999). It should be noted, however, that some classes of organic ligands (i.e., lipophilic organic ligands) form metal complexes that can be highly bioavailable to aquatic organisms (Dr. Jonathan Phinney, Center for Marine Conservation, Washington, D.C., Personal communication 1999).

Phytoplankton uptake and toxicity of copper and nickel are strongly influenced by water quality factors such as pH, alkalinity, hardness, dissolved organic matter, and suspended particulates, which affect the speciation and bioavailability of the metals. These variables determine the degrees of dissociation, complexation, and adsorption to particles, and therefore the availability of free metal ions and labile inorganic complexes, as well as competition with other cations for uptake sites on the cell membranes. In general, uptake rates and toxicity decrease with increases in any of these variables.

Metal uptake rates in phytoplankton depend on both the concentration of metal bound to the uptake sites and the rate of transfer across the cell membrane. The metal concentration at the uptake sites depends on the bioavailable metal concentrations in the water and the metal binding affinity of the transport sites. Since the number of membrane transport sites on a cell is generally fixed, the uptake rates reach maximums when all sites are saturated. This produces the typical saturation relationships for metal uptake rates as functions of concentration in water.

Metals are generally taken up by nutrient metal transport systems (Sunda and Huntsman, 1998). Since phytoplankton have specific nutrient requirements, they have cellular feedback mechanisms which allow them to regulate intracellular metal concentrations to levels that are optimal for growth and metabolism. This is accomplished by reducing their uptake rates when intracellular concentrations start to become excessive. The number of membrane transport proteins and their metal affinities are generally fixed, so uptake rates are regulated by controlling the transport rates across the cell membrane (Sunda and Huntsman, 1998). These transport rates are adjusted by feedback controls within the cell that regulate the activity of the membrane transport proteins in response to intracellular metal concentrations (Sunda and Huntsman, 1998). However, this control has a limited capacity, so excessive metal accumulation and resulting toxicity will occur when the capacity is exceeded. This results in the typical sigmoidal relationships of cellular metal accumulation with increasing metal concentrations in water (Sunda and Huntsman, 1998). Cellular metal concentrations increase with increasing bioavailable metal concentrations in water over the lower concentration range, then level off to much slower rates of increase as uptake rates become regulated, and finally increase at a faster rate as the regulatory capacity is exceeded. Regulation of copper accumulation also occurs in aquatic invertebrates and fish (Sorensen, 1991; Borgmann et al., 1993).

The metal transport proteins on the cell membranes are designed to bring nutrient metals into the cells. However, they are not entirely specific to single metals, so other metals with similar physicochemical characteristics can enter the cell through the same transport system. This produces competition for uptake sites between different metals in the water. This competition also extends further to processes within the cell, for example, to competition for binding sites on metalloproteins, or on intracellular control sites that regulate the activity of the membrane transport proteins (Sunda and Huntsman, 1998). Therefore, uptake rates could be reduced both

by the presence of competing metal ions external to the cell (competition for binding sites on the membrane), as well as by the accumulation of competing metals inside the cell, which further reduces uptake rates through feedback control of transport kinetics at the cell membrane (Sunda and Huntsman, 1998).

Competitive interactions can be toxic or protective, depending on the circumstances. For example, high copper concentrations could reduce the uptake of a critical nutrient metal, such as manganese, producing growth inhibition due to manganese nutritional deficiency. On the other hand, high manganese concentrations could inhibit copper uptake and prevent copper toxicity at copper concentrations that would normally be toxic. This situation could currently be occurring in South San Francisco Bay (Bruland, personal communication, 1999). Competitive interactions with copper are known to occur between manganese, zinc, and iron (Sunda and Huntsman, 1998). In addition, Reuter, et al (1981) suggests that elevated concentrations of silica in San Francisco Bay have an antagonistic relationship to the toxic effects of copper on diatoms. Competitive interactions also occur with nickel but they are less well known.

Toxic effects on phytoplankton are typically measured in terms of reductions in growth rates. Therefore, toxicity can be produced both by nutritional deficiencies in competing nutrient metals, and by the accumulation of excess toxic metals, which disrupt the normal metabolism of the cell. Toxicity from excess metals can occur through the displacement of other nutrient metals from their metabolic sites, through substitution in critical metalloproteins, which disrupts their metabolic functions, or through other toxic mechanisms. Excessive concentrations of several metals typically increases toxicity through additive effects if the modes or sites of toxic action are similar, or through increased stress to the phytoplankton cell even if they are not similar. However, as discussed above, competitive interactions can sometimes reduce toxicity by reducing uptake of a metal that would otherwise be toxic.

Phytoplankton have three major mechanisms for reducing toxicity when exposed to excessive concentrations of toxic metals such as copper and nickel. First, they produce phytochelatin, which binds the metals inside the cells and stores them in a nontoxic form (Ahner and Morel, 1995; Ahner et al., 1995). Second, some phytoplankton excrete organic cellular exudates at elevated copper concentrations, which chelate copper ions surrounding the cell, reducing copper bioavailability and uptake rates (McKnight and Morel, 1979; Van den Berg et al., 1979). Third, efflux systems are induced in some phytoplankton when intracellular metal concentrations become elevated to actively excrete accumulated metals from the cells (Sunda and Huntsman, 1998). However, all of these mechanisms have a limited capacity for detoxification, so toxic effects will occur when their capacity is exceeded. In addition, these detoxification pathways can sometimes reduce intracellular concentrations of competing nutrient metals, resulting in nutrient deficiencies from these other metals (Sunda and Huntsman, 1998).

### 4.4.1.3 Free Ionic Copper and Nickel Concentrations in Lower South San Francisco Bay

Copper and nickel uptake rates, cellular concentrations of the metals, and toxic effects are proportional to the free ion concentrations of the metals. The free ion is a measure of the bioavailability of a metal, and shows better correlation with uptake and toxicity than the previously used total dissolved metal concentrations. However, the free metal ions are not

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necessarily the only bioavailable or toxic forms. For a particular salinity or water quality condition, the free ion is proportional to other species such as labile inorganic complexes that may also be bioavailable. Therefore, the sum of all inorganic species should have the same correlation with uptake and toxicity as the free ion concentration. However, the free ion is currently more useful for assessing uptake and toxicity since uptake rates and toxic effects have been correlated with free ion concentrations in several recent studies.

Free ion concentrations were estimated for the average copper and nickel concentrations in Lower South San Francisco Bay in the Conceptual Model Report (Tetra Tech, 1999). They were determined using the speciation results of Donat et al. (1994) to estimate the total inorganic species, and the geochemical model MINTEQ to estimate the inorganic complexation and free metal ion concentrations. In South San Francisco Bay, the inorganic copper species are 8 to 20% of the total dissolved copper, and the inorganic nickel species are 50 to 66% of the total dissolved nickel (Donat et al., 1994). The midpoints of these ranges, 14% and 58%, respectively, are used in the following calculations of the free ionic concentrations of copper and nickel in Lower South San Francisco Bay.

The average total dissolved copper concentration in Lower South San Francisco Bay is 3.3  $\mu$ g/l during the dry season and 2.4  $\mu$ g/l during the wet season (Tetra Tech, 1999). Assuming 14% of the total dissolved copper is present as free ion and inorganic copper species, the concentrations of the inorganic species are about 0.46  $\mu$ g/l and 0.34  $\mu$ g/l during the dry and wet seasons, respectively. Based on MINTEQ model calculations, about 4.8% of the inorganic species is free copper ion during the dry season and about 2.3% is free ion during the wet season. Therefore, the free copper ion concentrations are approximately 0.022  $\mu$ g/l and 0.0077  $\mu$ g/l during the dry and wet seasons, respectively.

The average total dissolved nickel concentration in Lower South San Francisco Bay is 3.8  $\mu$ g/l during the dry season and 2.9  $\mu$ g/l during the wet season (Tetra Tech, 1999). Assuming 58% of the total dissolved nickel is present as free ion and inorganic nickel species, the concentrations of the inorganic species are about 2.2  $\mu$ g/l and 1.7  $\mu$ g/l during the dry and wet seasons, respectively. Based on MINTEQ model calculations, about 15% of the inorganic species is free nickel ion during the dry season and about 8% is free ion during the wet season. Therefore, the free nickel ion concentrations are approximately 0.33  $\mu$ g/l and 0.13  $\mu$ g/l during the dry and wet seasons, respectively. Free nickel concentrations are about 15 times higher than the free copper concentrations during the dry season, and about 17 times higher during the wet season.

# 4.4.1.4 Limitations on Using Free Ion Concentrations for Setting Site-Specific Objectives for Copper and Nickel in the Lower South San Francisco Bay

Free metal ion concentrations provide a better measure of phytoplankton uptake and toxicity than total dissolved metal concentrations since they include speciation and complexation effects. However, there are several important practical limitations to using free ion concentrations for setting site-specific objectives for copper and nickel in the Lower South San Francisco Bay. These reasons are 1) complexities of copper and nickel speciation, 2) relative inaccessibility of measurement equipment and required analytical expertise and high cost of analyses, and 3) the

lack of available data for free metal ion concentrations in the Lower South San Francisco Bay. These issues are discussed in greater detail in Section 4.4.5 of this report.

### 4.4.2 Sensitivity of Phytoplankton to Copper and Nickel

Phytoplankton uptake and toxicity from copper and nickel exposure are extremely important in the Lower South San Francisco Bay for several reasons. Phytoplankton have been reported to be among the most sensitive organisms to copper toxicity, phytoplankton form the base of the food chain and therefore support all of the higher trophic levels, and accumulation of metals is the major route of entry into the rest of the food chain. Several peer-reviewed articles (Table 4-12) were compiled and used as information sources. The following sections describe the sensitivity of phytoplankton to copper and nickel in laboratory tests using both laboratory dilution water and ambient Lower South San Francisco Bay water.

### 4.4.2.1 Phytoplankton sensitivity to copper

The number of individual phytoplankton species that have been tested to determine their sensitivities to copper is somewhat sparse even though copper is a well known algicide and herbicide. The U.S. EPA Ambient Water Quality Criterion for Copper (1985a) includes only ten test results for phytoplankton. The toxicological literature provides sensitivity data from several additional tests. Many of these tests used either non-standardized testing procedures or test endpoints and could not be included in the U.S. EPA Criterion Document. It should be noted, however, that the results from these tests are valid and can be used as additional information in the assessment.

When comparing algal toxicity data to either ambient conditions or water quality criteria/objectives, it is important to understand how algae respond to toxicity and how that toxicity is reported. Payne and Hall (1979) distinguished three responses of laboratory microalgal populations to toxicants: 1) reduced population growth (the most commonly reported test endpoint), 2) the algistatic response in which cell division is halted but the cells are not killed, and 3) the algicidal response in which cells are killed by the toxicant. The concept of algistasis is important to toxicology because algal populations exposed to some toxicants in the field may simply be attenuated and not lost (Thursby et al. 1993). These populations could recover if the effect of the toxicant is transitory and the population is not reduced significantly by herbivores (Thursby, et al. 1993).

The results of tests in laboratory water indicate that algal toxicity to copper has been observed to either affect cellular growth or photosynthetic rate in ranges that extend from a low of 4.6  $\mu$ g/L to a high of 8,000  $\mu$ g/L (Appendix D). Copper toxicity values are reported for six phytoplankton species that are either reside in the Lower South Bay (*Skeletonema costatum*) or have representative genera in the Lower South Bay (*Thalassiosira aestevallis*, *T. pseudonana*, *Nitzschia closterium*, *Prorocentrans micans*, and *Chlorella stigmatophora*). *Skeletonema costatum* had a 14-day cellular growth rate EC<sub>50</sub> of 50  $\mu$ g/L copper; *T. aestevallis* (reduced chlorophyll-a EC<sub>50</sub> = 19  $\mu$ g/L); *T. pseudonana* (72-hour cellular growth rate EC<sub>50</sub> = 5  $\mu$ g/L); *N. closterium* (96-hour cellular growth rate EC<sub>50</sub> = 33  $\mu$ g/L); *P. micans* (5-day cellular growth rate EC<sub>50</sub> = 10  $\mu$ g/L); and *C. stigmatophora* (21-day cell volume EC<sub>50</sub> = 70  $\mu$ g/L).

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## Table 4-12 Phytoplankton Toxicity Literature Compiled for this Impairment Assessment

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Metaxis and Lewis (1991) reported that *S. costatum* grew well in copper concentrations up to 0.4 uM (25.4 μg/L). Ristenbil and Wijnholds (1991) reported that cells of the South Bay diatom *Ditylum brightwellii* adapted to dissolved copper of 200 nM (12.7 μg/L). Metaxis and Lewis (1991) found that *Nitzschia thermalis* grew in copper concentrations up to 0.5 uM (31.8 μg/L). Toxicity values are also known for *Dunaliella tertiolecta*, a green flagellate, and *Phaeodactylum tricornutum*, a diatom, which are grown as food items for cultured zooplankton. *Dunaliella tertiolecta* was unaffected by copper concentrations of 8,000 μg/L (Abalde, et al. 1995). The more sensitive diatom, *P. tricornutum*, was unaffected by a copper concentration of 50 μg/L (Cid, et al. 1995). It is important to note that the results indicated above were based on tests performed in a variety of laboratory waters receiving different degrees of nutrification.

The above mentioned laboratory test results reported the sensitivities of various phytoplankton species to dissolved copper concentrations. More recently, toxicologists have recognized the importance of free ionic concentrations of metal as being more "bioavailable" and thus more toxic. This understanding is based on equilibrium partitioning of the metal of concern with various natural and anthropogenic chelators or ligands and has been addressed in Section 4.4.1 of this report.

Several studies (Sunda and Guillard, 1976; Brand, et al. 1986; Bruland, et al. 1991; Moffett and Brand, 1996) have reported on the sensitivity of several classes of phytoplankton (cyanobacteria, coccolithophores, dinoflagellates, and diatoms) to free ionic copper. These classes of phytoplankton were found to exhibit reduced growth at free ionic copper concentrations as low as approximately  $10^{-11}$  M (approximately 0.6 ng/L, or pCu = 11, where pCu is the negative log of the molar concentration of the cupric ion) with the cyanobacteria being the most sensitive to free ionic copper concentrations followed in order of decreasing sensitivity by coccolithophores, dinoflagellates, and diatoms. In addition, they found that, in the absence of external chelators, naturally occurring concentrations of free ionic copper in upwelled oceanic water may be great enough to inhibit the reproduction of some phytoplankton species, especially cyanobacteria.

The studies by Sunda and Guillard (1976) and Brand, et al (1986) provide the basis for the current understanding of phytoplankton response to free ionic copper. Sunda and Guillard (1976) for the diatom, *T. pseudonana* and Brand, et al (1986) for the cyanobacteria, coccolithophores, dinoflagellates, and diatoms (including *T. pseudonana*). The other studies cited above use the toxicity information provided by Sunda and Guillard (1976) and Brand, et al (1986).

Sunda and Guillard (1976) reported that the diatom, *T. pseudonana* exhibited reduced reproduction at free ionic copper concentrations of 2.5 x 10<sup>-11</sup> M (0.002 μg/L; pCu = 10.6) and complete cessation of growth at free ionic copper concentrations greater than 5 x 10<sup>-9</sup> M (0.3 μg/L; pCu = 8.3). Brand, et al (1986) performed a more comprehensive evaluation of the sensitivities of different classes of phytoplankton (cyanobacteria, coccolithophores, dinoflagellates, and diatoms (including *T. pseudonana*). Of the phytoplankton species that were tested, three of the diatom species and one genera are residents of the Lower South Bay (*Ditylum brightwellii, Rhizosolenia setigera, Skeletonema costatum*, and *Thalassiosira* spp. (*T. oceanica* and *T. pseudonana*)) (Cloern 1996). These results (Table 4-13) are in agreement with those presented by Sunda and Guillard (1976) for *T. pseudonana*.

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Table 4-13
Inhibition of Phytoplankton Reproduction Rates by Copper

Experiment	Algal Group	No. Species/Isolates	pCu for 50% Inhibition in Reproduction Rate		
			Mean <u>+</u> SD	Range	
1	Diatoms	13	10.04 <u>+</u> 0.29	9.45-10.47	
	Neritic	8	10.02 <u>+</u> 0.28	9.45-10.47	
	Oceanic	5	10.06 <u>+</u> 0.28	9.53-10.32	
1	Coccolithophores	5*	10.43 <u>+</u> 0.24*	9.5-10.65	
	Neritic	1	10.18		
	Oceanic	4	10.49 <u>+</u> 0.23	10.17-10.65	
	E. huxleyi		9.5		
1	Dinoflagellates**	1	11.10		
2	Dinoflagellates	9	10.40 <u>+</u> 0.44	9.82-11.07	
	Neritic	4	10.64 <u>+</u> 0.31	10.35-11.07	
	Oceanic	5	10.20 <u>+</u> 0.39	9.82-10.86	
1	Cyanobacterium**	1	10.94		
2	Cyanobacteria	7	10.88 <u>+</u> 0.44	10.25-11.54	
	Neritic	5	10.77 <u>+</u> 0.44	10.25-11.54	
	Oceanic	2	11.13		

(From: Brand, et al. 1986) \* Excluding *E. huxleyi* 

The mean sensitivities of the different phytoplankton species indicate a general trend with the cyanobacteria appearing to be most sensitive to free ionic copper concentrations, followed in sensitivity by the dinoflagellates, coccolithophores, and diatoms. However, when one examines the range of the responses to free ionic copper concentrations, the distinction is not so well defined (Table 4-14). There appears to be overlap between the observed toxicity responses between the different phytoplankton classes. Examining the more relevant neritic species (neritic = zone between the edge of the continental shelf and the shore), we see that cyanobacteria exhibited 50% reduction in reproduction rate at free ionic copper concentrations ranging from  $0.0002 - 0.004 \,\mu\text{g/L}$ ; the dinoflagellates ranged from  $0.0005 - 0.003 \,\mu\text{g/L}$ ; there was only one neritic coccolithophore value of  $0.004 \,\mu\text{g/L}$ ; and the diatoms ranged from  $0.002 - 0.02 \,\mu\text{g/L}$ . The value reported by Sunda and Guillard (1976) for T. pseudonana was in agreement with the findings of Brand, et al (1986), with the EC<sub>50</sub> being  $0.002 \,\mu\text{g/L}$ .

Ambient site water tests have been performed using the copper sensitive diatom T. pseudonana. S.R. Hansen & Associates (1992) tested the sensitivity of T. pseudonana to copper in Lower South Bay waters. In this study, five test results were obtained for the South Bay and Dumbarton Bridge site waters, stations that are within the boundaries of this assessment. The chronic values (geometric mean of the NOEC and LOEC) reported for T. pseudonana ranged from 4.2-41.4  $\mu g/L$ , with a geometric mean of  $13.2 \mu g/L$  dissolved copper.

<sup>\*\*</sup> Oceanic species

Table 4-14
Inhibition of Neritic Phytoplankton Reproduction Rates by Copper

		50% Inhibition in Reproduction Rate (μg/L)			
Experiment	Algal Group	Mean	Range		
1	<b>Diatoms</b> T. pseudonana*	0.006 0.002	0.002 - 0.02 0.002		
1	Coccolithophores Emiliana huxleyi	0.004 0.02	0.004 0.02		
2	Dinoflagellates	0.0013	0.0005 - 0.003		
2	Cyanobacteria	0.001	0.0002 - 0.004		

(From: Brand, et al. 1986) \*Sunda and Guillard (1976)

The dissolved copper concentrations that have been reported for the Lower South Bay between 1989 and 1999 are graphically represented in Figure 4-1. This figure indicates that, with the exception of the one chronic value of 4.2 ppb¹, even the greatest measured concentration of dissolved copper was well below the concentration of copper in ambient Lower South Bay water that produced a toxic response by the copper sensitive diatom, *T. pseudonana*. This comparison is important for two reasons. First, *T. pseudonana* is one of the most sensitive phytoplankton species to copper (U.S. EPA 1985a). Second, these data were derived from tests conducted directly in Lower South Bay site waters and therefore, are critical in assessing whether any suggested site-specific water quality objectives will be protective of aquatic plants in the Lower South Bay.

### 4.4.2.2 Phytoplankton sensitivity to nickel

Data on the toxicity of nickel to phytoplankton is very sparse. In fact, the most recent U.S. EPA Ambient Water Quality Criteria for Nickel (1986) reports that there have been no phytoplankton toxicity tests that meet the standard toxicity testing requirements. They do, however, report the results from several toxicity tests that were performed under non-standard testing conditions. These tests used *T. pseudonana*, a species known to be very sensitive to other metals (e.g., copper). The test endpoint reported was the concentration of nickel that caused a 65% reduction in chlorophyll-a production. These test results indicate that *T. pseudonana* is sensitive to nickel concentrations between 17 and 140  $\mu$ g/L and that the toxicity response is directly proportional to the test salinity.

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<sup>&</sup>lt;sup>1</sup> The chronic value of 4.2 was produced during the same testing event where *T. pseudonana* exhibited an ultrasensitive response to copper in laboratory water. This value (1.7 μg/L) was much lower than other values observed for this species in laboratory water for all subsequent tests. As a result, any of the toxicity values that were obtained during this testing event should be used judiciously.

A comparison between the sensitivity of T. pseudonana as reported from laboratory water tests (U.S. EPA 1986) to ambient concentrations of dissolved nickel in the Lower South Bay between 1989 and 1999 (Figure 4-2). This figure indicates that ambient concentrations of dissolved nickel have been greater than the minimum  $EC_{50}$  value (17  $\mu$ g/L) once since 1989 and that that event occurred between 1990 and 1991. It should be noted, that these toxicity values are based on the sensitivity of T. pseudonana to nickel in laboratory water that contained little or no metal complexing ability. This provides an additional measure of safety because it does not take into consideration the ability of the ambient Lower South Bay waters to complex nickel, reducing its bioavailability and subsequent toxicity to aquatic plants.

### 4.4.3 Phytoplankton Species Composition in the Lower South San Francisco Bay

An increasing concern regarding the status of the South Bay Ecosystem in general, and sensitive phytoplankton species in particular has become an important issue in determining whether the Lower South San Francisco Bay is currently impaired by copper and nickel. This concern is based on three points: 1) the measurements of free ionic copper in the Lower South San Francisco Bay as reported by Donat, et al (1994), 2) the sensitivities of phytoplankton reported by Brand, et al (1986), and 3) reported depauperate populations of copper sensitive phytoplankton classes (e.g., cyanobacteria, coccolithophores, and dinoflagellates) and zooplankton species (i.e., *Acartia tonsa*) in the Lower South Bay.

These concerns may be based on the belief that there is an extensive amount of phytoplankton data for the South Bay and that the South Bay phytoplankton community has been fully characterized. Jim Cloern, however, has indicated that this is not the case (USGS, personal communication, 1998). According to Jim Cloern, the plankton populations are difficult to monitor, and the South San Francisco Bay does not have a comprehensive plankton monitoring program that can support a full characterization of baseline trends in plankton assemblage status. There have been however, some studies conducted to characterize the South Bay phytoplankton community structure (Cloern, et al 1985; Cloern 1996). Cloern, et al (1985) and Cloern (1996) report that several classes of phytoplankton are commonly observed during the annual spring blooms. However, Cloern (1996) does not provide the criterion required for a phytoplankton species to be listed as "commonly observed". Cloern, et al. (1985) defines commonly observed phytoplankton species as those comprising > 10% of the biomass.

A common annual cycle for the phytoplankton community in the South Bay consists of a large spring bloom of diatoms, a summer bloom of small flagellates, dinoflagellates, and diatoms, and an autumn bloom of dinoflagellates (Smetacek 1986; Tett et al. 1986; Mallin, et al. 1991). Cloern (1984) reported a similar annual cycle with increased diatom abundance in the spring consisting of *Thalassiosira* spp., *S. costatum*, *Cyclotella caspia*, and *Leptocylindricus danicus*. Cloern (1984) further reported that the summer-fall communities were dominated by microflagellates consisting of *Chroomonas* spp., *Cryptomonas* sp., and *Pyramimonas* spp. A recent enumeration of phytoplankton samples taken from 1992 through 1995 lists 40 common species (Cloern 1996). Of these, 22 were diatoms (Class Diatomophyceae) representing 11 genera. The remainder were from the class Chlorphyceae (4 species from 3 genera), Chrysophyceae (3 species from different genera), Cryptophyceae (3 species from 1 genus),

Dinophyceae (5 species from different genera), Prasinophyceae (2 species from different genera), and one photosynthetic ciliate (Table 4-15).

While Cloern (1996) did not report the presence of any cyanobacteria or coccolithophore species to be commonly present in the Lower South Bay, he did find the cyanobacterium (*Synechococcus*) to be present in all samples collected from all cruises between April and August 1998 (Jim Cloern, USGS, Personal communication 1999 Manuscript in press). Additionally, Brian Palenik (UCSD) has found several species of cyanobacteria to be present at concentrations up to 50,000 cells/ml in the South Bay in July 1999. These concentrations are similar to levels observed to occur in Southern California coastal waters. Palenik reports cyanobacteria concentrations to be near the detection limits during the January and April 1999 sampling events in the South Bay. These studies indicate that cyanobacteria are present in the South Bay during seasonal periods when copper concentrations are greatest. The complete texts to these reports are presented in Appendix G to this report.

Of additional interest is the presence of the dinoflagellate, *Prorocentrum minimum* in the South San Francisco Bay (Cloern, 1996). This dinoflagellate genus has been reported by Brand, et al (1986) as being one of the more sensitive dinoflagellates to free ionic copper concentrations, exhibiting reduced reproduction rates and death at pCu values of 12 and 10.5 and concentrations of 0.000063 and  $0.002~\mu g/L$ , respectively. It should be noted, however, that if the ambient free ionic copper concentrations of  $0.013~\mu g/L$  reported by Donat, et al (1994) are typical for the Lower South San Francisco Bay, these organisms would not be expected to be commonly found in the South Bay.

The presence of cyanobacteria and dinoflagellate genera in the South Bay that are sensitive to elevated concentrations of free ionic copper would indicate that other factors that have not been taken into consideration are occurring in the South Bay. As mentioned previously, the toxicity of free ionic copper can be ameliorated by the presence of competing ions like zinc, iron, and manganese (Sunda and Hanson 1987; Moffett, et al 1997; Hutchins, et al 1999). Moffett, et al (1997) reports that zinc has been shown to ameliorate copper toxicity to several ciliates and in the diatom *T. pseudonana*, presumably by competing with uptake sites on the cell membrane.

The need to better understand the processes that determine species composition of phytoplankton blooms is underscored by several recent discoveries. For instance, it has been demonstrated that some diatom species produce a potent chemical inhibitor of copepod egg development (Poulet et al 1994). A diet of *Thalassiosira rotula*, a diatom common in the South Bay, significantly reduced egg production and hatching success in the copepod, *Acartia clausi* compared to a diet of *Prorocentrum minimum*, a dinoflagellate, also common to the South Bay (Ianora et al 1996). This may also help to explain the absence or near-absence of another copepod, *Acartia tonsa* from the Lower South Bay. *Acartia tonsa* has been reported by Sunda, et al (1987) to be sensitive to free ionic copper activities of pCu = approximately 10. Further, Metaxes and Lewis (1991) tested the response of copper to two diatoms, *Skeletonema costatum* (common to the South Bay) and *Nitzschia thermalis* (genus common to the South Bay), when grown together in mixed culture. *Skeletonema costatum* exhibited growth retardation at three copper concentrations (i.e., 6.4, 25.4, and 31.8 ppb) in the presence of *N. thermalis*, while it was only affected at the highest copper concentration when grown alone.

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Table 4-15
Phytoplankton Species Commonly Observed During Blooms in South San Francisco Bay

Class	Species
Diatomophyceae (Diatoms)	Chaetoceros debile
	C. decipiens
	C. didymus
	C. gracilis
	C. socialis
	C. vistulae
	C. wighami
	Coscinodiscus curvatulus (Actinocyclus
	curvatulas)
	C. lineatus (Thalassiosira leptopus)
	C. radiatus
	Cyclotella meneghiniana
	Cyclotella sp.
	C. striata
	Ditylum brightweilli
	Eucampia zoodiacus
	Leptocylindrus minimus
	Nitzschia seriata (Pseudo-nitzschia seriata)
	Paralia sulcata
	Rhizosolenia setigera
	Skeletonema costatum
	Thalassiosira decipiens (T. angulata)
	T. rotula
Chlorophyceae (Green Algae)	Chlorella marina
omorophyodao (Groom Augao)	C. salina
	Monoraphidium convolutum
	Nannochloris atomus
	Training atomac
Chrysophyceae (Small flagellates)	Chromulina sp.
	Kephyrion sp.
	Ochromonas sp.
Cryptophyceae (small flagellates)	Chroomonas acuta (Teleaulax acuta)
orypropriyodad (siriali liageliates)	C. amphioxeia (T. amphioxeia)
	C. salina
	C. Saina
Dinophyceae (Dinoflagellates)	Gonyaulax tamarensis (Alexandrium ostenfeldii)
	Heterocapsa triquetra
	Katodinium rotundatum
	Prorocentrum minimum
	Protoperidinium claudicans
Prasinophyceae (small flagellates)	Pyramimonas micron (P. orientalis)
Taomophyodae (omaii nageliates)	Tetraselmis gracilis
	Toti aseittiis graciiis
Photosynthetic ciliates	Mesodinium rubrum

(From: Cloern, 1996)

It is unlikely that a single algal species would be commercially or ecologically important as might be the case with a fish or invertebrate species (Mount 1992). Several phytoplankton species may be equally good for primary production and oxygenation, and the protection of desirable phytoplankton as a group should be the goal for protecting beneficial uses (Mount 1992). Cloern (1996) has provided ample evidence that the South San Francisco Bay is not depauperate of primary producers (Table 4-15). In addition, Cole and Cloern indicated that in 1993, primary productivity in the South San Francisco Bay was approximately three times greater than the primary productivity present in the adjacent Central San Francisco Bay; more than four times greater than primary productivity in San Pablo Bay; and almost twenty times the primary productivity in the Suisun Bay (1997, USGS Web page http://sfbay.wr.usgs.gov/access/ColeCloern/HumphMap.html). This indicates that there is

http://sfbay.wr.usgs.gov/access/ColeCloern/HumphMap.html
This indicates that there is adequate primary productivity occurring in the Lower South Bay to support the beneficial uses of the South Bay ecosystem.

It is unknown what effect the greater presence of the introduced benthic filter-feeding asiatic clam, *Potamocorbula amurensis* in the northern stretches of the San Francisco Bay may or may not have on primary productivity in those regions of the Bay. Algal blooms in the Lower South Bay occur when the water column is stratified and normal convection currents keep the phytoplankton suspended in the upper portion of the water column, effectively keeping the algal cells from contact with the benthic filter-feeders. If this same process occurs in the northern portions of the Bay, the effect that the benthic filter-feeders have on primary productivity would be minimal. If, on the other hand, vertical stratification of the water column plays a minimal role in the bloom dynamics in the northern reaches of San Francisco Bay and phytoplankton are exposed to the benthos, then the presence of a large number of benthic filter feeders could be expected to play a significant role in primary productivity. Additional studies on Bay-wide bloom dynamics are required before this issue can be addressed with any certainty.

### 4.4.4 Use of Phytoplankton as an Indicator of Beneficial-Use Impairment

Experimental studies show that the toxicity of copper to phytoplankton is controlled by both its bioavailability and its competitive interactions with essential metals. The fact that environmental differences in copper speciation affect its bioavailability is widely appreciated. For example, complexation by strong organic ligands renders copper(II) much less toxic, while complexes with lipophilic organic ligands could make copper (II) more bioavailable. It is less commonly realized that the effects levels of copper on phytoplankton generally increase with increasing concentrations of essential metals in the growth medium (or environment). For manganese and zinc, such an interaction with copper has been demonstrated. It is likely that both copper speciation and competition for essential metals affect copper toxicity to phytoplankton in South San Francisco bay.

Figure 4-12 compares the ranges of copper, zinc, and manganese concentrations from toxicity experiments where growth inhibition was demonstrated with the ranges of these metals measured in both South San Francisco Bay and in other estuarine and oceanic environments. The metal concentrations are reported as the negative logs of the free ion concentrations (e.g., pCu, pZn, pMn). As noted above, the free ion concentration is used because it is the measure of

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bioavailable metal concentration that is most commonly reported in experiments that consider speciation effects on metal toxicity.

pCu varies from greater than 12 (very low [Cu<sup>2+</sup>]) in open ocean waters to 9.7 in South San Francisco Bay (Donat et al., 1994), a greater than 200-fold variation. The fraction of the total dissolved copper present as free cupric ion, or Cu<sup>2+</sup> ion, varies depending on the concentrations of inorganic and organic complexing agents (metal-binding ligands). These ligands compete for Cu<sup>2+</sup> with sites on the cell that transport copper into the cell. Thus, copper toxicity is inversely related to the concentrations and affinities of ligands that bind it. Free Cu<sup>2+</sup> comprises only about 5% of the inorganic copper complexes present in seawater. When organic ligands are present, it comprises an even smaller fraction of total dissolved copper.

Inhibition of phytoplankton growth in laboratory studies has been observed to start at pCu's of 10 to 11, or [Cu<sup>2+</sup>] greater than 10<sup>-11</sup> M to 10<sup>-10</sup> M (Brand et al., 1986). The direct measurements of pCu in the South Bay noted above, although limited in number, suggest that copper toxicity could influence phytoplankton growth in South San Francisco Bay.

However, there are important exceptions that raise questions about the general utility of the Brand et al. (1986) study to predict toxic effects of Cu<sup>2+</sup> in South San Francisco Bay. In particular, the presence of the diatom *T. pseudonana* in the bay, despite the predicted inhibition of growth at a pCu of 10.0, suggests that either pCu is quite variable or that it is less toxic under some circumstances. Observations of cyanobacteria and the dinoflagellate *Prorocentrum minimum* in the bay suggest the same. Whether this suggests a shortcoming of the free cupric ion concept or some other factor is an important issue both for scientists and regulators.

As noted above, other laboratory studies (Sunda and Huntsman, 1998) conducted using the same chelator-amended medium methodology used by Brand et al. (1986) have shown that the concentrations of zinc (as Zn<sup>2+</sup>) and manganese (as Mn<sup>2+</sup>) in the media strongly influence the effects levels for Cu<sup>2+</sup>. Thus, if Zn<sup>2+</sup> and Mn<sup>2+</sup> levels in the bay are higher than the levels used in the Brand et al. (1986) study, it is likely that higher concentrations of Cu<sup>2+</sup> are required in order to observe toxicity. In fact, the laboratory study was conducted at relatively low concentrations of these metals, pZn of 10.3-10.6 and pMn of 8.3 to 8.7 (Figure 4-12).

Although neither pZn nor pMn have been reported for South San Francisco Bay in the literature, a reasonably good case can be made that both Mn and Zn occur at higher levels in the bay than in the Brand et al. (1986) study. Total dissolved Zn concentrations of 7-28 nM have been measured in the South Bay (Flegal et al., 1991). Although Zn complexation measurements in the bay have not been published, there is no reason to think that Zn is strongly complexed. Zn complexation by generic humic substances is weak. Results from the open ocean, where the concentration of strong zinc chelators has been measured at 1 nM (Bruland et al., 1991), suggest that it is likely that the concentrations of strong chelators in the South Bay are insufficient to significantly bind Zn. Thus, if we assume that essentially none of the Zn is organically-complexed, we may assume that 63% of the dissolved (inorganic) Zn occurs as the free ionic species (Byrne et al., 1988). The resulting pZn range of 8.4-7.8 indicates that [Zn²+] concentrations in the South Bay are at least two orders of magnitude above the levels used in the Cu²+ toxicity experiments (Figure 4-12).

We are not yet aware of any Mn concentrations reported for San Francisco Bay. However, in the recent reviews of Sunda (1991), the estuarine range of pMn is reported to be 7.9 to 6.3 (Figure 4-12). Again, these are well above the pMn levels used in the Brand et al. (1986) study. Thus, it is also possible that competitive inhibition by Mn also reduces the toxicity of Cu to otherwise sensitive species in the bay.

While demonstrating that high zinc and manganese concentrations explain the discrepancy between predictions and observations of copper toxicity in South San Francisco Bay requires further experimental studies, it is worthwhile to note that they are founded on the same body of experimental studies as the suggestion of  $Cu^{2+}$  toxicity. In other words, it would be inconsistent to adopt the  $Cu^{2+}$  toxicity approach and not include the competitive interactions of Zn and Mn. A resolution of this issue for South San Francisco Bay could be obtained by a combined field and laboratory study. In the field study, one would measure pCu, pZn and pMn in the bay. In the lab study, one would measure the effects levels for  $[Cu^{2+}]$  at levels of pZn and pMn closer to those observed in the bay.

### 4.4.5 Uncertainties and Resolving Uncertainties

The consequences of the decisions that are made regarding the setting of site-specific objectives extend well into the future. For this reason, it is essential that predictions of the effects of allowable concentrations of copper and nickel in Lower South San Francisco Bay are accurate. However, the presence of uncertainty complicates the ability to make accurate predictions of environmental effects. Furthermore, without a measure of the magnitude of the uncertainty associated with decision criteria, decision-makers are unable to effectively weigh and use the results of environmental analyses. These issues are addressed in the impairment assessment by making a vigorous effort to identify the magnitude and sources of uncertainty associated with each of the indicators that are used in the impairment assessment and that are used in the development of alternatives for site-specific objectives.

Uncertainty is defined herein as the state or condition of incomplete or unreliable knowledge. For each indicator evaluated or analysis conducted in this assessment, both the sources and the magnitude of known uncertainties are identified. The sources include natural variability, sample variability, and the appropriateness of models that are used in making predictions. Ideally, the magnitudes of identified uncertainties are addressed using descriptive statistics and by setting confidence limits on predicted values. In the absence of quantitative information, a professional judgement of the value of the existing information is presented.

The uncertainties that are associated with this indicator are listed below:

**Uncertainty -** Uncertainty is introduced during phytoplankton testing because the test media requires filtration and addition of nutrients. This makes the results difficult to interpret. It is generally unknown what effect filtration and nutrient addition has on metals bioavailability. In addition, some phytoplankton are known to have the ability to produce phyto-chelators that can reduce the toxicity of metals.

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Resolving this Uncertainty - Better characterization of ambient site and laboratory water will help resolve the questions surrounding the effects of filtration and nutrification. This will provide knowledge about the constituents of the "apparent complexing capacity" (natural and anthropogenic ligands and ionic competition) and how they are affected by removal (via filtration) and nutrification. The actual role of phyto-chelators and the ability of phytoplankton to produce them needs to be studied in greater detail. This ability to produce compounds that can reduce metals toxicity is very important in understanding the actual sensitivity of phytoplankton to copper and nickel.

**Recommended Action -** Characterize the constituents that comprise the "apparent complexing capacity" present in both the ambient Lower South San Francisco Bay and laboratory waters. Additional studies are required to better quantify the causes of phytochelatin production, the quantities produced, and their effects on reducing copper and nickel toxicity to resident phytoplankton species.

Uncertainty - Direct usage of the phytoplankton toxicity results presented by Brand, et al (1986) and Sunda and Guillard (1976) to predict the potential for toxicity to occur to phytoplankton in the Lower South San Francisco Bay does not take into consideration site-specific water quality characteristics. Several studies mentioned previously in this report have identified other metal ions that compete with copper for cellular binding sites, thus reducing copper toxicity to phytoplankton (e.g., zinc, manganese, silica, and iron). Concentrations of these competing ions in the test solutions used by Brand, et al (1986) and Sunda and Guillard (1976) were lower than those reported to be present in the Lower South San Francisco Bay, thus causing uncertainty in the ability to predict phytoplankton toxicity based on free ionic copper measurements alone.

**Resolving this Uncertainty -** This uncertainty can be reduced by performing combined field and laboratory studies. In the field study, one would measure pCu, pZn, and pMn in the Lower South San Francisco Bay. The laboratory study would focus on measuring the effects levels for the cupric ion concentration at levels of pZn and pMn that more closely resemble what is found in the Lower South San Francisco Bay.

**Recommended Action** – Perform field and laboratory toxicity testing to determine the effects of ambient pZn and pMn concentrations on the toxicity of copper to phytoplankton.

**Uncertainty -** There is uncertainty in assuming that phytoplankton are equally, or less sensitive to copper and nickel than animal species. Current water quality objectives are based on animal species, with the assumption that they would also be protective of phytoplankton species.

**Resolving this Uncertainty -** Additional testing to characterize the sensitivity of phytoplankton to copper and nickel will provide information regarding the effects

of copper and nickel on the phytoplankton community. If existing water quality objectives aren't protective of the phytoplankton community, a new set of studies would be required and a new site-specific water quality objective determined.

**Recommended Action -** Perform toxicity tests exposing resident phytoplankton species to dissolved concentrations of copper and nickel in both lower South San Francisco Bay and laboratory waters over the course of an entire season.

#### 4.4.6 Conclusions

There are currently more data gaps in the phytoplankton database than in any of the others that are being used in this assessment. However, the importance of the phytoplankton community to the overall beneficial uses of Lower South San Francisco Bay indicates that it must be addressed.

Such an important component of the Lower South San Francisco Bay's beneficial uses requires that the information used in any assessment be beyond criticism. Currently, the information that is being used to assess the health of the phytoplankton community in Lower South San Francisco Bay is outdated and inadequately characterized. Only additional characterization of this community's sensitivity to copper and nickel will assure that it, and the beneficial uses of Lower South San Francisco Bay are adequately protected.

Adequate protection can be obtained by characterizing the phytoplankton community structure, its sensitivity to free ionic and dissolved concentrations of copper and nickel, and characterization of the components of the apparent complexing capacity of Lower South San Francisco Bay waters. These would:

- Characterize the phytoplankton community structure by providing information about species succession, and whether the presence or absence of a species affects overall succession. If sensitive species are not being protected, and they are important in the overall succession of Lower South San Francisco Bay phytoplankton species', the resultant community may exhibit impairment;
- Assessing the sensitivities of the phytoplankton to free ionic and dissolved forms of copper and nickel will provide information that can be used to determine whether ambient concentrations of those metals are potentially harmful; and
- Improved characterization of the apparent complexing capacity of ambient Lower South San Francisco Bay water will 1) aid in the interpretation of toxicity test results; 2) increase understanding the processes that control the bioavailability of copper and nickel; and 3) allow for improved management decisions when, or if, the components of the ambient apparent complexing capacity change.

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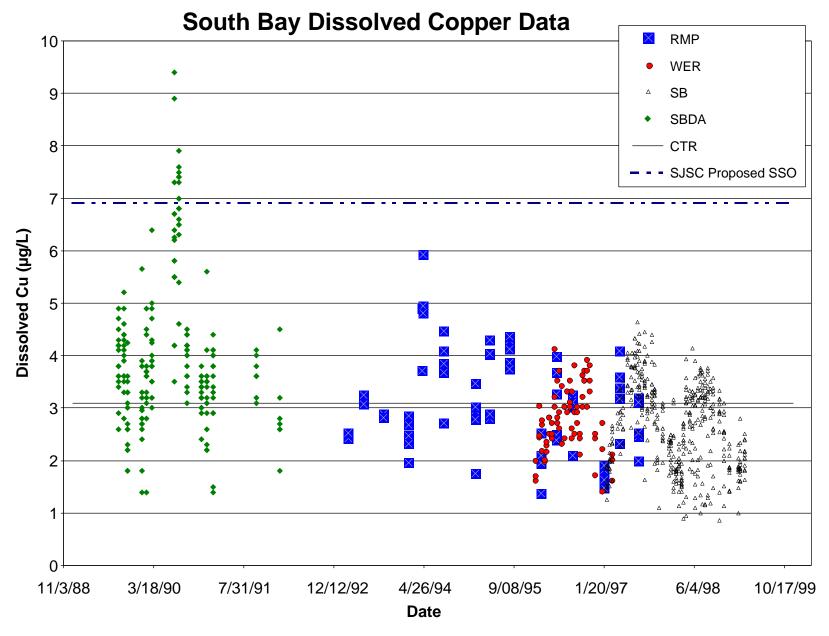


Figure 4-1. Dissolved copper concentrations in Lower South San Francisco Bay between 1989 and 1999 compared to the proposed water quality criteria values for copper.

### **South Bay Dissolved Nickel Data**

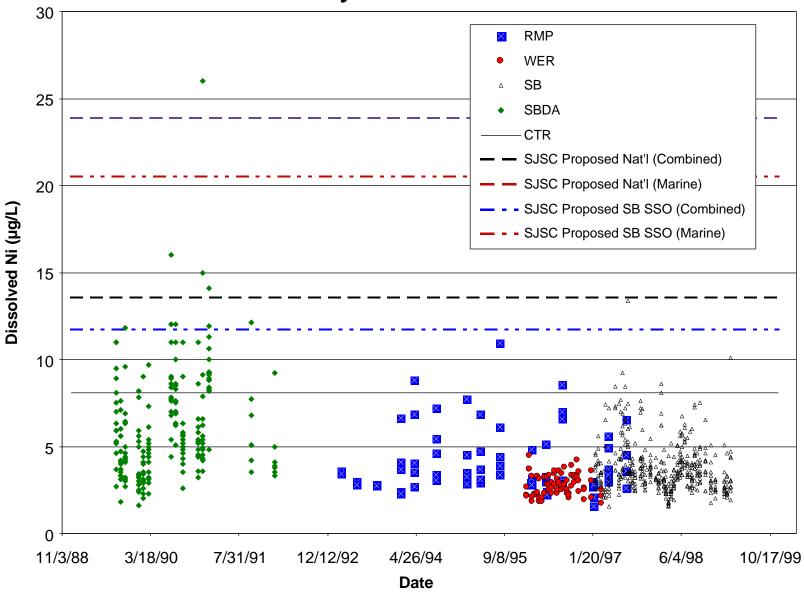


Figure 4-2. Dissolved nickel concentrations in Lower South San Francisco Bay between 1989 and 1999 compared to the national water quality criterion and San Francisco Bay Water Quality Objective, and SJSC proposed dissolved nickel water quality criterion values.

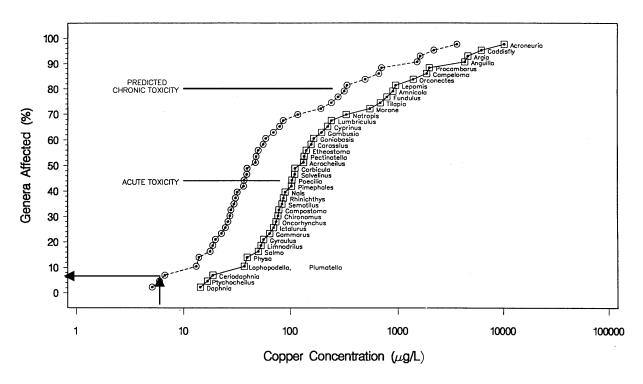
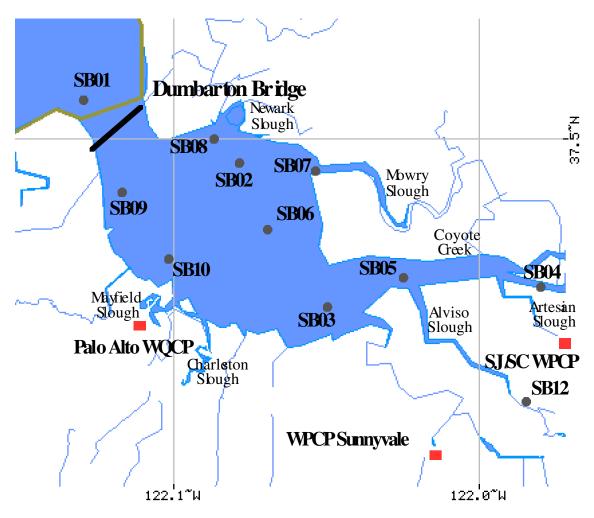


Figure 4-3. Example AERAP output using U.S. EPA acute freshwater copper toxicity database.



SBS SITES	REFERENCE LOCATIONS	LONGITUDE	LATITUDE	RMP SITES
SB01	Channel Marker #14	122.08.60W	37.30.48N	BA30
SB02	Channel Marker #16	122.05.04W	37.29.59N	BA20
SB03	Channel Marker #18	122.03.01W	37.27.27N	BA10
SB04	CC Railroad Bridge	121.58.64W	37.27.59N	C-3-0
SB05	LEM site in Coyote Creek	122.01.48W	37.27.84N	
SB06	Between Channel Markers #17 & 18	122.04.30W	37.28.52N	
SB07	Mouth of Mowry Slough	122.03.27W	37.29.54N	
SB08	Mouth of Newark Slough	122.05.41W	37.29.92N	
SB09	Mouth of Mayfield Slough	122.07.08W	37.27.06N	
SB10	Mouth of Charleston Slough	122.05.99W	37.28.19N	
SB11	Standish Dam in CC	121.55.29W	37.27.10N	BW10
SB12	Alviso Yacht Club Dock	121.58.45W	37.25.34N	BW15

South San Francisco Bay site map showing the location of 11 of the 12 stations sampled in the South Bay Study (SBS). Site SB11 located at Standish Dam in Coyote Creek is not within the range of the map presented. The above table indicates analogous sites from the Regional Monitoring Program.

Figure 4-4. Map of monitoring station locations in Lower South San Francisco Bay.

### **Aquatic Community Risk Model (Chronic)**

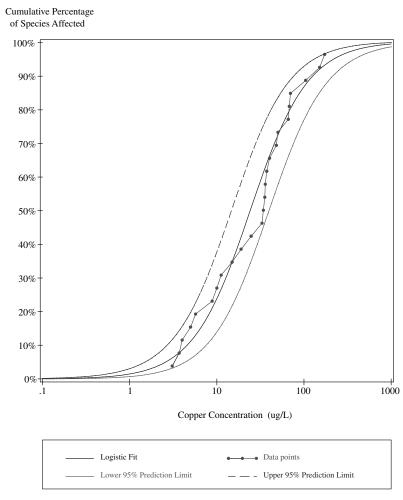


Figure 4-5. Logistic regression for chronic effects of copper on San Francisco Bay species.

### **South Bay Total Copper Data** 110 RMP 100 WER SB 90 SBDA - SF SSO 80 70 Total Cu (µg/L) 60 50 40 30 20 10 0 -3/18/90 7/31/91 12/12/92 4/26/94 9/8/95 1/20/97 11/3/88 6/4/98 10/17/99

Figure 4-6. Total copper concentrations in Lower South San Francisco Bay between 1989 and 1999 compared to the San Francisco Water Quality Objective for copper.

Date

### **South Bay Dissolved Copper Data**

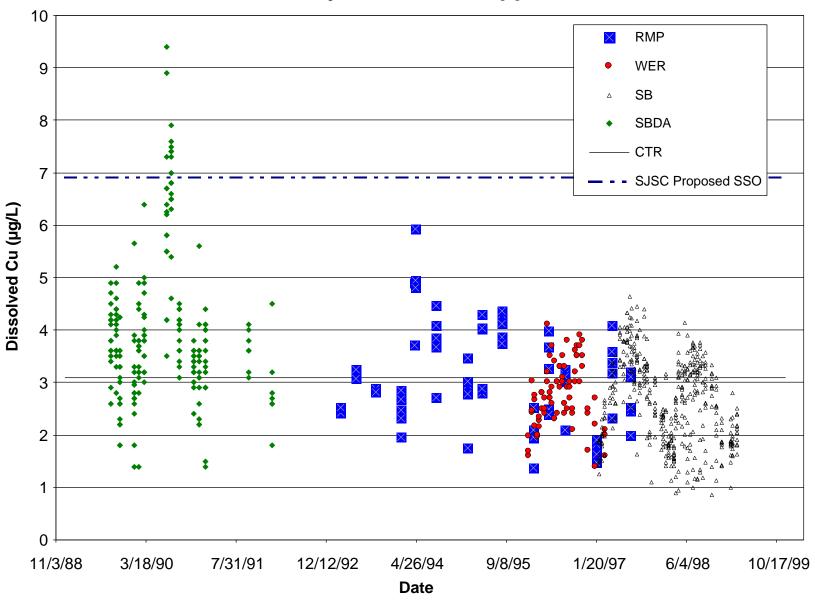


Figure 4-7. Dissolved copper concentrations in Lower South San Francisco Bay between 1989 and 1999 compared to the National Water Quality Criterion for copper and the SJSC proposed SSO for copper.

### **South Bay Dissolved Nickel Data** 30 RMP WER SB 25 **SBDA CTR** SJSC Proposed Natn'l (Combined) 20 SJSC Proposed Nat'l (Marine) Dissolved Ni (µg/L) SJSC Proposed SB SSO (Combined) - SJSC Proposed SB SSO (Marine) 15 10 5

Figure 4-8. Dissolved nickel concentrations in Lower South San Francisco Bay between 1989 and 1999 compared to the National Water Quality Criterion for nickel and the SJSC proposed SSO values for nickel.

4/26/94

**Date** 

9/8/95

1/20/97

6/4/98

10/17/99

0 <del>↓</del> 11/3/88

3/18/90

7/31/91

12/12/92

### **Chronic Toxicity Compared to a Range of EEC**

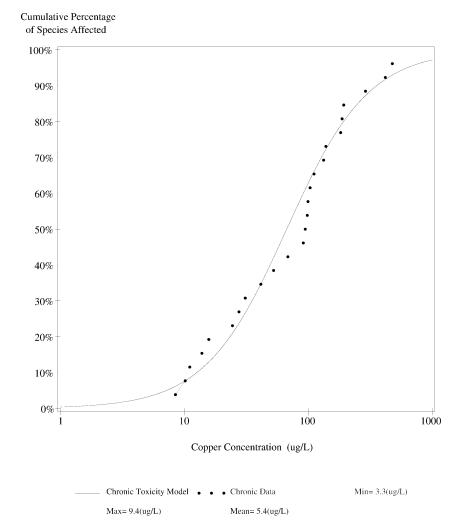


Figure 4-9. Logistic regression for chronic effects of copper on San Francisco Bay species compared to the ambient EEC during the dry season.

### **Chronic Toxicity Compared to a Range of EEC**

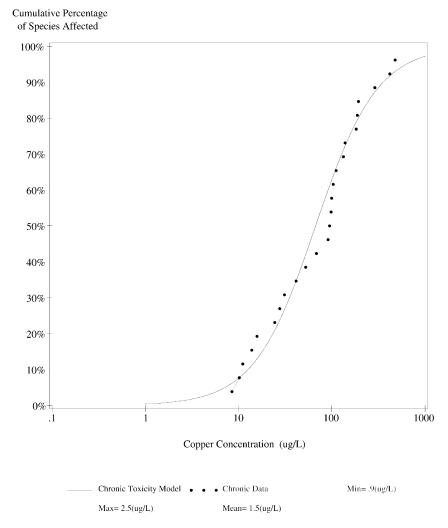


Figure 4-10. Logistic regression for chronic effects of copper on San Francisco Bay species compared to the ambient EEC during the wet season.

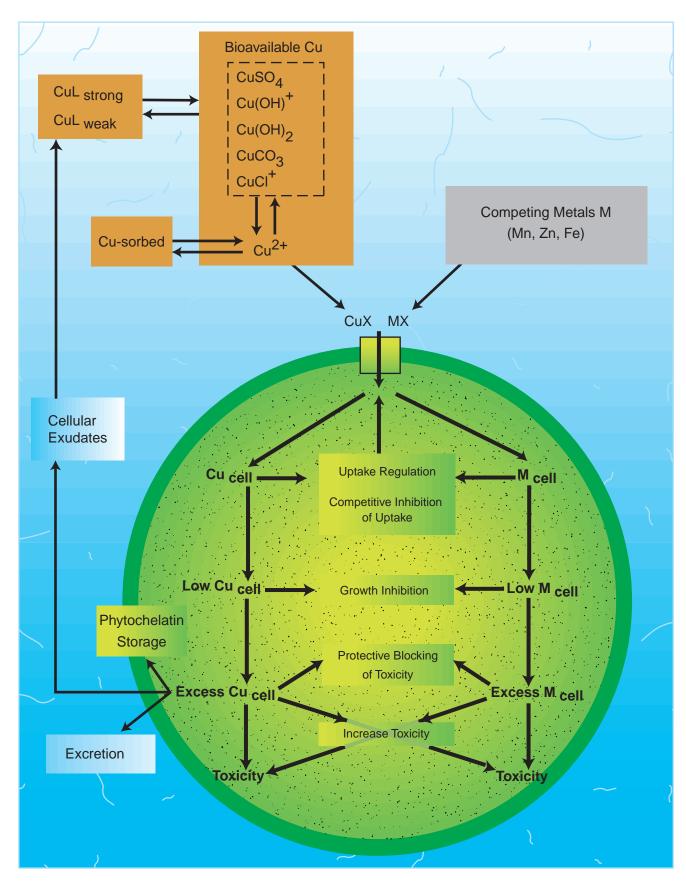


Figure 4-11. Copper uptake and toxicity in phytoplankton.

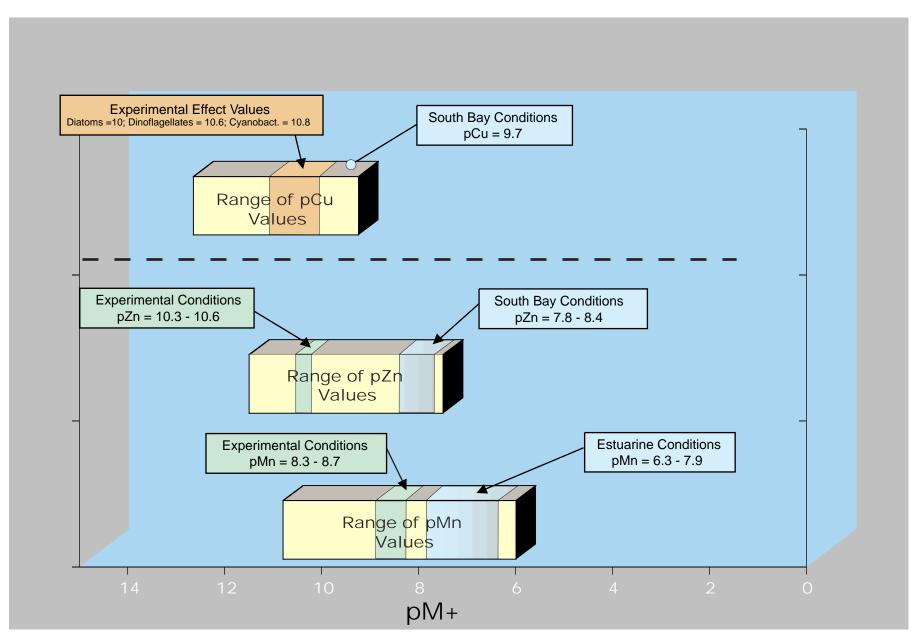


Figure 4-12. Range of pM<sup>+</sup> values in oceanic and estuarine environments.

## 5.0 IMPAIRMENT ASSESSMENT: SYNTHESIS AND RECOMMENDATIONS

This impairment assessment was conducted to provide information necessary to help stakeholders evaluate whether or not beneficial uses are currently being impaired in Lower South San Francisco Bay. The assessment results are a direct result of efforts made to accomplish five goals:

- 1. Compile and evaluate data on ambient concentrations and toxicity information for copper and nickel in the Lower South San Francisco Bay
- 2. Identify, evaluate and select indicators of beneficial-use impairment
- 3. Develop endpoints for the selected indicators that can be used to assess the existence of impairment and compare these values to ambient concentrations in Lower South San Francisco Bay
- 4. Assess the level of certainty with which it can be shown ambient concentrations of copper and nickel are or are not resulting in beneficial-use impairment
- 5. Recommend numeric values for the TMDL Work Group to consider as site-specific objectives for dissolved copper and nickel in Lower South San Francisco Bay

The impairment assessment relies on a "weight of evidence" technical approach. Following this "weight-of-evidence" approach, all available evidence is reviewed and incorporated in proportion to its applicability, technical certainty, statistical validity, etc. in evaluating the likely impacts and impairment of beneficial uses. In general "suites" of indicators are believed to be better indicators of ecosystem health and impairment than single indicators/organisms. This approach is consistent with EPA's 305(b) guidance regarding "integrated assessment." The indicators and lines of evidence used in this assessment synthesis are described in Sections 2, 3, and 4 of this report.

The following potential conclusions and outcomes to the beneficial use impairment assessment were considered as part of developing the impairment assessment findings.

- No impairment: A finding of no impairment requires a high level of certainty regarding assessment results. The lines of evidence and indicators would unequivocally demonstrate no negative impact to Beneficial Uses due to copper and nickel. In addition, the lines of evidence and indicators would affirm ecosystem integrity and a quantitative assessment of the status of Beneficial Uses under current and projected (within the current permitting cycle) loading of copper and nickel. This finding would be based on a large quantity of documented data for multiple lines of evidence and or indicators, each providing consistent results.
- **Impairment unlikely**: This finding requires clear support from more than one line of evidence and is based on a substantial amount of laboratory and or environmental data. This level of finding does include uncertainties regarding the finding. It is

necessary to describe and define the consequences of identified uncertainties. It is also suggested that the uncertainties be addressed through recommended studies.

- Possible impairment: A possible impairment finding requires that a line of evidence
  or indicator suggests diminished ecosystem integrity that causes a negative impact on
  any designated Beneficial Use from copper or nickel. Possible impairment can be
  due to existing loadings or expected future loadings of copper or nickel. There are
  uncertainties associated with this finding that must be described with additional
  studies designed to confirm the existence and/or level of impairment.
- **Definite impairment**: The lines and evidence and indicators clearly indicate negative impact on designated Beneficial Uses due specifically to ambient concentrations of copper and nickel. There is substantial documented data to support the finding and there are few if any uncertainties associated with the assessment conclusion.
- Cannot determine impairment: This finding does not indicate impairment or non-impairment of the designated Beneficial Uses. The uncertainties are due to inadequate data, lack of knowledge regarding basic processes or status of resident aquatic life and wildlife populations. This finding requires a significant commitment of resources for monitoring and special studies to better determine the status of Beneficial Uses and the extent and magnitude of stressors (i.e., copper and nickel).

The assessment results are summarized separately for copper and nickel. The findings regarding the impairment assessment are presented and supported with a succinct summary of the available information. Next, the uncertainties that surround the findings for both copper and nickel are identified, and special studies that could be conducted to further improve our understanding of copper and nickel effects on beneficial uses are identified. Finally, recommendations are made for the development of site-specific water quality objectives for copper and nickel in Lower South San Francisco Bay and for updating the 303(d) listing.

### 5.1 Copper Impairment Assessment

Consistent with the potential conclusions and outcomes to a beneficial use impairment assessment that were previously presented to the TMDL Work Group, the following finding is technically supportable:

Impairment to the Beneficial Uses of Lower South San Francisco Bay due to ambient water column, sediment, and bivalve tissue copper concentrations is unlikely.

The following points, upon which the above finding is based, include indicators and lines of evidence that evaluate conditions in the water column (1, 2, 3, and 4), and in sediment and tissues (5). This is followed in Section 5.3 with a summary of the uncertainties that exist and the description of special studies that could be conducted to resolve these uncertainties.

An important component of the impairment finding is the extrapolation of laboratory toxicity data to the ambient environment. Water effects ratios (WER) are an important tool in reducing

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the uncertainty associated with the extrapolation of laboratory toxicity values to the ambient environment. Before reviewing the impairment assessment findings the following review of the WER values used in this assessment is provided. The Water Effects Ratio (WER) method of the Indicator Species Procedure was used to derive a site-specific water quality criterion for dissolved copper for Lower South San Francisco Bay. These methods allow for modifications to the national criterion by using a site-specific multiplier, which accounts for ambient water quality characteristics that may affect the bioavailability of copper. The results of this work support the WER values ranging from 2.77 to 3.5 and corresponding site-specific water quality objective values [i.e., Criteria Continuous Concentration (CCC) values] ranging from 6.9 to 8.8  $\mu$ g/L dissolved copper.

The results of the WER studies were reviewed by Dr. Glen Thursby (U.S. EPA, Narragansett, RI). Dr. Thursby found that the data used in these analyses "were valid and as good as any I have seen for toxicity tests" and that the authors built in a lot of conservatism within the various steps along the way."

1. The first line of evidence is a conservative screening analysis that is based on the assumption that if the most sensitive species is not impacted by concentrations of dissolved copper in Lower South San Francisco Bay, the remainder of the ecosystem will not be impacted. The information for this line of evidence comes from the toxicity database that was developed for resident species in Lower South San Francisco Bay. The finding is that concentrations of dissolved copper in the water column do not exceed chronic toxicity values for the most sensitive species that have been tested in Lower South San Francisco Bay.

Copper toxicity data were compiled for 26 resident species of Lower South San Francisco Bay. The lowest toxicity value was the Criteria Continuous Concentration (CCC) for the larval stage of the mussel *Mytilus edulis* (2.52  $\mu$ g/L dissolved copper laboratory <sup>1</sup>). To compare this CCC value in a meaningful way to ambient waters it is necessary to account for the apparent complexing capacity of Lower South San Francisco Bay waters that reduces the bioavailability (and toxicity) of dissolved copper. The measure of the apparent complexing capacity is expressed as a water effects ratio (WER), and the laboratory CCC is multiplied by this value. A conservative WER value for Lower South San Francisco Bay is 2.77 -- the adjusted CCC is 6.9  $\mu$ g/L (i.e., 2.5 x 2.77 = 6.9). Comparison of this toxicity value with the ambient water quality data collected by the City of San Jose at 11 stations between February 1997 and March 1999 shows that this CCC value was not exceeded in any sample (408 total samples). The maximum value recorded in the ambient monitoring program was 4.9 µg/L. In other words, the study performed by the City of San Jose (1998) found that the most sensitive species (M. edulis) was unaffected in ambient Lower South San Francisco Bay water containing dissolved copper concentrations less than 6.9 µg/L. Thus indicating that ambient dissolved copper concentrations in the Lower South San Francisco Bay did not exceed 6.9  $\mu$ g/L and were protective of *M. edulis*.

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This CCC value is based on updated dissolved copper toxicity tests performed on *Mytilus edulus* as part of the City of San Jose's study, "Development of a Site Specific Water Quality Criterion for Copper in South San Francisco Bay." The updated tests found a Final Acute Value (FAV) of 7.88 μg/L that was divided by the national acute to chronic ratio (ACR) of 3.127. The national FAV for *Mytilus edulis* is 8.5 μg/L, the CCC is 2.7. The CCC value selected is the most conservative possible because the lowest laboratory results were used and the highest ACR was applied.

- 2. The Aquatic Ecological Risk Assessment Protocol was used to develop a community-based environmental risk criterion (ERC) for dissolved copper that is protective of 95% of the resident and surrogate taxa in Lower South San Francisco Bay. The estimated ERC is 3.1 μg/L, which is a laboratory toxicity value without application of a WER. The WER adjusted ERC is 8.6 μg/L. Based on the comparison with the City of San Jose's water-quality database, this value was not exceeded in any of the samples (408 total samples). Further statistical comparison of ambient or expected environmental concentrations (EECs) to the 5% ERC at 12 Lower South San Francisco Bay stations showed that the observed differences between these values was not statistically significant.
- 3. The National database lists the non-native macroalga *Champia parvula* as being sensitive to dissolved copper concentrations as low as 4.6 µg/L. The most sensitive native algal species (*Thalassiosira pseudonana*) has a reported sensitivity to dissolved copper concentrations as low as 5 µg/L. Both of these species exhibit sensitivities to dissolved copper that are greater than the ERC value of 3.1 µg/L generated by AERAP. This indicates that an ERC value that is based on the sensitivity of an animal species (*Mytilus edulis*) to copper would be protective of aquatic algal species. In addition, the most sensitive phytoplankton organisms (cyanobacteria) have been found to be present in the Lower South San Francisco Bay. This is further evidence that phytoplankton populations are not being impaired by ambient copper concentrations in Lower South San Francisco Bay.
- 4. Lower South San Francisco Bay ambient waters are routinely monitored for chronic water column toxicity to aquatic organisms. Chronic water column toxicity in the Lower South San Francisco Bay has been rarely observed. Copper has never been attributed as the cause of any observed toxicity.
  - There are three main sources of ambient Lower South San Francisco Bay toxicity data. The first and most extensive is the data collected by the San Francisco Bay Regional Monitoring Program (RMP). The RMP has reported that no observed ambient chronic toxicity has occurred in the Lower South San Francisco Bay since quarterly monitoring began in 1993. The other two studies were performed in order to establish site-specific water quality objectives for copper in San Francisco Bay (S.R. Hansen & Associates 1992 a) and in Lower South San Francisco Bay (Larry Walker Associates et al. 1991 a, b). They report only one instance of ambient toxicity occurring. This was to the diatom *Thalassiosira pseudonana* and copper was not deemed the causative agent.
- 5. The RMP and the USGS (Hornberger et al, 1998; Luoma et al, 1998) have routinely measured copper concentrations in Lower South San Francisco Bay bivalve tissues. The USGS study has established a direct linkage between elevated sediment and bivalve tissue copper concentrations, and reduced bivalve reproductive capacity. However, the USGS study also demonstrated that an area that was once heavily impacted by an elevated sediment copper concentration is no longer impacted by copper.

The USGS studies report that between the late 1970s and the late 1980s the clam population that occurred on a mudflat near the City of Palo Alto's POTW outfall was severely impacted by the presence of elevated concentrations of copper in the local sediments. Sediment copper concentrations have decreased by 50% between 1979 and 1993, with a high of 86 ppm

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(1979) to a minimum of 43 ppm (1993). During approximately the same period, bivalve tissue copper concentrations were reduced by an order of magnitude, with a high of 295 ppm (1979) to a minimum of 24 ppm (1991). Bivalve reproductive capability was closely associated with sediment and tissue copper concentrations, with less than 20% of the individual clams being reproductively active between 1974 and 1983. As sediment and tissue copper concentrations began to decrease, 70-100% of the clam population became reproductively active with reproductive patterns typical of less impacted sites not being observed until clam tissue copper concentrations reached 35 ppm. A comparison study (Luoma et al 1998) using clams collected from a mudflat near the San Jose POTW outfall has demonstrated clam tissue copper concentrations are similar to those currently observed at the Palo Alto POTW outfall. This study suggests that a region of the Lower South San Francisco Bay that was once highly impacted by copper is no longer impacted.

### 5.2 Nickel Impairment Assessment

The results of the impairment assessment for nickel support the following finding:

Impairment to the Beneficial Uses of Lower South San Francisco Bay due to ambient nickel concentrations is unlikely

The following points are the basis for this finding. In Section 5.3 the uncertainties are identified, and special studies for resolving these uncertainties are described.

1. A combination of the indicator species and recalculation procedures was used to develop site-specific modifications to the national water quality criterion for nickel. The recalculation of a water quality criterion for total and dissolved nickel resulted in ranges from 11.89 to 24.42  $\mu$ g/L and 11.65 to 23.93  $\mu$ g/L, respectively. Using the 1989-1999 water quality database as a basis of comparison, the lower limit on this range was exceeded once out of the 794 samples collected during that time period. No measurements have been reported to be greater than the higher limit of the range.

The supporting studies were specially designed acute and chronic flow-through bioassay tests that were conducted using three marine species (topsmelt fish, *Atherinops affinis*; red abalone, *Haliotes rufescens*; and mysid shrimp, *Mysidopsis intii*). All three species are from the west coast, with the topsmelt being a native species to the Lower South San Francisco Bay. These results were reviewed by Dr. Glen Thursby of the EPA's Narragansett, R.I. Laboratory. In his report to EPA Region 9, he found that the species and methodologies that were used in this work were appropriate for developing site-specific modifications to the national water quality criterion for nickel.

2. The site-specific case studies for San Francisco Bay and Lower South San Francisco Bay have demonstrated that the toxicity of nickel is less in ambient site-water than the national water quality criteria predict. And, as such, the amount of bioavailable nickel is reduced by the presence of components which make up the apparent complexing capacity of Lower South San Francisco Bay. These components either bind with nickel, making it biologically unavailable (e.g., natural or anthropogenic organic ligands) or compete for receptor sites on, or in, the organism (e.g., manganese and iron). It is believed that the

national criteria for nickel are over-protective of the beneficial uses of Lower South San Francisco Bay.

### 5.3 Uncertainties and Special Studies

The findings of the impairment assessment for both copper and nickel are not unequivocal. Several key uncertainties exist that stakeholders may wish to resolve, and the special studies described below are an integral component of the assessment findings. The purpose of these studies would be to reduce the identified uncertainties and to provide a more complete understanding of the existing information on the toxicity of copper and nickel and the biogeochemical processes that affect ambient concentrations and bioavailability. The three primary areas of uncertainty are the toxicity of copper to phytoplankton, copper and nickel cycling in Lower South San Francisco Bay, and sediment toxicity.

Unnecessary study duplication will be prevented or reduced by including all current and future studies that have objectives that overlap those of the special studies provided in this report. These studies will be identified and, if possible, the data will be used to address the key concerns associated with the Lower South San Francisco Bay TMDL Study.

#### 5.3.1 Phytoplankton Toxicity

There appears to be an inconsistency in the phytoplankton toxicity data reviewed in the impairment assessment. Moreover, a specific concern has been raised among the TMDL Work Group members and other stakeholders regarding the effects of existing ambient copper concentrations on the most sensitive species of phytoplankton.

On the one hand there is information on the toxicity of copper to phytoplankton that suggests existing ambient concentrations of dissolved copper (average concentration ~ 3.1 µg/L; maximum concentration =  $4.9 \mu g/L$ ) are not toxic to sensitive phytoplankton species. There are three lines of evidence to support this determination. The first is the U.S. EPA Ambient Water Quality Criterion for Copper (1984) which reports on the results of laboratory toxicity tests for ten phytoplankton species. The results of these tests indicate that algal toxicity to copper ranges from an Effects Concentration at which 50% of the population is impacted from approximately 5 μg/L to 50 μg/L. Five of these test species are reported to reside in Lower San Francisco Bay. The second line of evidence is the results of toxicity tests using ambient water from Lower South San Francisco Bay and the most sensitive phytoplankton species listed in the national data set: the diatom, Thalassiosira pseudonana. S.R. Hansen & Associates (1992a) found that the chronic values (the geometric mean of the No-Observable Effects Concentration (NOEC) and the Lowest-Observable Effects Concentration (LOEC) ranged from a low of 8.4 µg/L to a high of 53.3 µg/L. The third line of evidence is the sensitivity of *T. pseudonana*. In the studies described below, T. pseudonana was found to be as sensitive to free ionic copper concentrations as the cyanobacteria, cocolithophores, and dinoflagellates.

These studies that indicate that existing ambient concentrations of dissolved copper are not toxic to sensitive phytoplankton classes are not consistent with results reported by Brand, et al (1986) and a number of other researchers (Bruland, et al 1991; Moffett and Brand 1996; and Sunda and

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Guillard 1976) that show that certain cyanobacteria, cocolithophores, dinoflagellates, and diatoms (e.g., T. pseudonana) exhibit reduced growth when free ionic copper concentrations 10<sup>-11</sup> M (6 x 10-5 μg/L) in seawater having little or no organic complexing capacity and low concentrations of competing ions (i.e., zinc, manganese, and iron). Moreover, recent calculations presented in a companion report (Conceptual Model Report, Tetra Tech 1999) indicate that free ionic copper concentrations in this range can occur in the Lower South San Francisco. However, direct usage of the phytoplankton toxicity results presented by Brand, et al. (1986) and Sunda and Guillard (1976) to predict the potential for toxicity to occur to phytoplankton in the Lower South San Francisco Bay does not take into consideration sitespecific water quality characteristics. Several studies mentioned previously in this report have identified other metal ions that compete for cellular binding sites with copper and resulting in reducing copper toxicity to phytoplankton (i.e., zinc, iron, silica, and manganese). Concentrations of these competing ions in the test solutions used by Brand, et al (1986) and Sunda and Guillard (1976) were lower than those reported to be present in the Lower south San Francisco Bay, thus causing uncertainty in the ability to predict phytoplankton toxicity based on free ionic copper measurements alone.

**Key Uncertainty:** Phytoplankton are among the most sensitive organisms to copper and are an important consideration in the impairment assessment. However, little direct information is available on the toxicity of copper to phytoplankton under the specific water quality and speciation conditions in Lower South San Francisco Bay.

**Special Study:** This uncertainty can be reduced by performing combined field and laboratory studies. In the field study, one would measure pCu, pZn, and pMn in the Lower South San Francisco Bay. The laboratory study would focus on measuring the effects levels for the cupric ion concentration at levels of pZn and pMn that more closely resemble what is found in the Lower South San Francisco Bay.

### 5.3.2 Biogeochemical Processes Influencing Speciation

One of the findings of the Conceptual Model Report (Tetra Tech 1999) was the need for a better understanding of copper and nickel speciation in Lower South San Francisco Bay. This finding is reiterated here with an emphasis on the importance of achieving a better understanding of copper and nickel bioavailability.

**Key Uncertainty:** It is difficult to predict the variability that can be expected in the apparent complexing capacity of the waters in Lower South San Francisco Bay. Speciation data are available for only a few sampling dates. The components of the apparent complexing capacity are fairly well known. However, seasonal and annual variability in the individual contributions to the overall apparent complexing capacity and their temporal variations are not. An improved understanding of the factors contributing to apparent complexing capacity could contribute to better anticipation of potential shifts in individual components that may affect apparent complexing capacity.

**Study Approach:** Additional studies should be considered to improve understanding of copper and nickel speciation in the South Bay. There are several key factors that influence copper and nickel bioavailability. In general, free metal ions, lipophilic organic, and inorganic complexes

are bioavailable for uptake by aquatic organisms and metals that are complexed with strong organic complexes are not bioavailable. There are three important exceptions to this, Fe(III)siderophore complexes for which specific cellular uptake mechanisms exist, lipophilic complexes that can passively diffuse through cell membranes, and colloidal metals which can be accumulated by filter-feeding organisms (J. Hering, personal communication, 1999). However, adsorbed forms and organic complexes make up a major portion of the total copper and nickel in the South Bay water column, and these forms are not bioavailable. Speciation and bioavailability of copper and nickel in South San Francisco Bay have been characterized in both the water column (Donat et al., 1994) and in tributary runoff and POTW loads (Sedlak et al., 1997; Bedsworth and Sedlak, 1999). Complexation with organic ligands plays a major role in the speciation. The ligands can be separated into two major classes, very strong ligands and weaker ligands. The sources and nature of the ligands have been characterized (Sedlak et al., 1997; Bedsworth and Sedlak, 1999). However, little is known about internal sources of ligands and the internal cycling and fate of organic ligands within the Bay, and how future changes in the discharge of these ligands could affect the complexation and speciation of the metals. The kinetics of the complexation reactions may also be important, since the slow kinetics suggested by Sedlak et al. (1997) and Bedsworth and Sedlak (1999) for the strong ligand classes may prevent the use of equilibrium-based geochemical models for accurate predictions of speciation. As a result of these uncertainties, studies that improve our ability to predict speciation and bioavailability as conditions in the water column change should receive high priority.

### 5.3.3 Sediment Toxicity

Copper concentrations are elevated in Lower South San Francisco Bay sediments relative to background concentrations. Average surficial sediment copper concentrations in the Lower South San Francisco Bay are 41 mg/kg, approximately twice the average background concentration of 20 mg/kg. Even so, it is extremely difficult to demonstrate that copper is the cause for any observed sediment toxicity.

The Lower South San Francisco Bay sediments are routinely monitored for toxicity to aquatic organisms (both benthic and planktonic). The most comprehensive source of sediment monitoring data comes from the San Francisco Regional Monitoring Program (RMP). The RMP has monitored Lower South San Francisco Bay sediments for toxicity twice annually since 1993. They have determined that the Lower South San Francisco Bay sediments are fairly consistently toxic to benthic amphipods, with their "South Bay" site exhibiting toxicity in 63% of the toxicity tests performed. Other studies performed by Larry Walker Associates (1991a, b) indicated that Lower South San Francisco Bay sediments were not toxic to aquatic organisms.

**Key Uncertainty:** There are currently no definitive methods that can be used to determine whether any observed sediment toxicity is caused by the presence of copper. Sediments are extremely complex and even though many of the components that make up the sediment are fairly well known, interactions between those components and copper remain unclear at this time.

**Study Approach:** No study approach is recommended at this time because of the current lack of any methodology that can be used to definitively assess the specific role that copper plays in any observed sediment toxicity. There is however, a U.S. EPA Sediment Toxicity Identification

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Evaluation (TIE) Guidance document that is nearing completion. This guidance document may provide procedures that can be used in future assessments to assess the causes of any observed sediment toxicity.

## 5.4 Recommendations for Site Specific Objectives for Copper and Nickel for South San Francisco Bay

A primary objective of this study was to develop site-specific objectives (SSOs) for copper and nickel for lower South San Francisco Bay. The purpose of this section is to present to stakeholders the range of values, considerations, and calculations used to develop recommended SSOs for dissolved copper and nickel in lower South San Francisco Bay.

There are three components of the site-specific objective values prepared for Lower South San Francisco Bay used in this study:

- 1. laboratory-measured toxicity values,
- 2. laboratory-measured water effects ratio, and
- 3. other supporting information.

The approach for both copper and nickel can be described in three steps:

- 1. Identify the range of values for environmental risk concentrations (ERCs) and water effects ratios (WERs) that bracket values that could be used in a SSO algorithm to develop recommendations.
- 2. Describe the factors that influence the range of indicator values. Consider those factors to select a best estimate for each indicator value that will be used in a SSO algorithm.
- 3. Apply the SSO algorithm to indicator values selected to develop a SSO recommendation.

Each of these components and steps and their role in developing the recommended SSOs will be described in the following pages.

### 5.4.1 Range of Values To Develop Site-Specific Objectives for Dissolved Copper

The first component of the SSO recommendation are laboratory-measured toxicity values. This study considers several toxicity values for use in developing SSO recommendations. Other toxicity values that are within the range generated as part of this study include:

- The California Toxic Rule (CTR) proposed value of 3.1 µg/L dissolved copper. The CTR was developed to be protective of 95% of taxa represented in U.S. EPA's national toxicity database.
- The City of San Jose conducted a repetition of the laboratory toxicity tests used to establish the CTR and developed an updated value of  $2.5 \mu g/L$ .

These values can be used to compare the range of toxicity values generated by the AERAP indicator.

There are two important factors that drive the range of indicator values for the AERAP ERC estimates. The ERC values are those concentrations of dissolved copper that are estimated to protect a specified percentage of community taxa. The first factor that influences the range of the ERCs is the sensitivity of the individual species that are included in the AERAP toxicity database. A logistic regression procedure is applied to the toxicity database to generate the cumulative frequency curve. The ERC is extrapolated from the curve after selecting the desired level of protection. The range of values in Table 5-1 were developed using four different toxicity databases and three different levels of protection for community taxa (i.e., 90%, 95%, and 99%).

The toxicity databases used to generate the values listed in Table 5-1 include:

- National / No Plants: This is the database used to develop the CTR value of 3.1 µg/L. The National database is composed of all species that are included in U.S. EPA's National Water Quality Criteria Dataset. This toxicity database includes the results of toxicity testing for all marine or salt-water species that have been developed and incorporated by EPA for use in developing national water quality criteria. The National / No Plants database include several species that are not resident to San Francisco Bay and are not commonly used as surrogates for San Francisco Bay. The EPA guidelines restrict the use of laboratory toxicity tests where the testing matrix (laboratory water) has been amended in any way. Laboratory tests on aquatic plants generally "condition" the water or testing matrix with phosphorus and or nitrogen to ensure that the lack of growth is not due to the absence of essential nutrients. Therefore, toxicity tests for phytoplankton are not included in setting national criterion. There are 28 species included in the National / No Plant database.
- U.S. EPA "WER Cookbook" Species Deletion Procedure: This database is a subset of the National Database that excludes nonresident species in accordance to the guidelines described in the U.S. EPA WER Cookbook (U.S. EPA, 1994). The species in this database represent 9 taxonomic families from various diverse ecological niches.
- **Resident and Surrogate:** This database excludes nonresident species and those not commonly used as surrogates for resident species for which no toxicity information exists. Surrogates are useful because they provide a more complete species assemblage than would otherwise be possible.
- **Resident:** The Resident toxicity database includes only those species that are resident in San Francisco Bay. For that reason the number of species in the database drops to sixteen. Representation of several ecological niches is also lost in the Resident toxicity database.

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The range of percentages for protection of community taxa of 90% to 99% extends beyond what should reasonably be considered for the development of SSOs. For example, guidelines provided by U.S. EPA recommend that water quality standards protect 95% of community taxa. The intent of the 95% guideline is to ensure that water quality standards contribute to the protection of a fully functioning ecological community. It is also unlikely that it is possible or beneficial to target the upper limit of the range of AERAP values (e.g., 99%). It is unclear whether any species resident to San Francisco Bay have sensitivities to dissolved copper at the ERC values estimated for the 99% level of community protection. However, the extremes help provide perspective on the values that should be considered for use in the SSO algorithm.

Table 5-1
Range of AERAP Environmental Risk Concentration Values

Ontions	Chronic Environmental Risk Concentration Values (µg/L)			Number of Species
Options	90%	95%	99%	in Database (N)
National/No	U95% = 8.4μg/L	U95% = $4.3 \mu g/L$	U95% = 1.0μg/L	
Plant	5.1μg/L	2.6μg/L	0.6μg/L	28
	L95% = 1.8μg/L	L95% = 0.9μg/L	$L95\% = 0.2\mu g/L$	
EPA WER	U95% = $6.3 \mu g/L$	U95% =3.5μg/L	$U95\% = 0.9 \mu g/L$	
Cookbook Species	4.0μg/L	2.2μg/L	0.6μg/L	14
Deletion	L95% = 1.8μg/L	L95% =0.9μg/L	$L95\% = 0.2\mu g/L$	
Resident and	U95% = 8.3μg/L	U95% =4.8μg/L	U95% = <b>1.4μg/L</b>	
Surrogate	5.4μg/L	3.1μg/L	0.9μg/L	20
	L95% = 2.5μg/L	L95% =1.3μg/L	$L95\% = 0.3 \mu g/L$	
Resident	U95% = 7.6μg/L	U95% = 4.1μg/L	$U95\% = 1.1 \mu g/L$	
	4.2μg/L	2.2μg/L	0.5μg/L	13
	L95% = 0.8μg/L	L95% =0.3μg/L	$L95\% = 0.0 \mu g/L$	

The Water Effects Ratio (WER) is another key component of the SSO recommendation and there are several factors that affect the range of WERs. The primary variable that must be considered in evaluating a WER is the sensitivity of the species used in the study. Table 5-2 presents the range of possible WER values that could be calculated based on whether all three Lower South San Francisco Bay sites were used or just the two northern most stations were used. The WER value obtained from the San Mateo Bridge site is included for data completion. In selecting the range of WERs that are listed in Table 5-2 the technical project team included values that were developed using the most sensitive species in the Resident and Surrogate toxicity database, the larval life-stage of *Mytilus edulis* (blue mussel). Other factors important to consider for evaluating WERs developed from site-specific studies are the location and number of sampling points within South Bay, the frequency of sampling, and the length of the sampling period. The location and number of samples is important to fully characterize the water quality conditions in lower South San Francisco Bay. The length of the sampling period is important to characterize any seasonal or temporal effects on the WER.

The geometric mean values for WERs that are listed in Table 5-2 were developed during the Lower South San Francisco Bay Copper Site-Specific Study (City of San Jose 1998). The WERs

calculated at the Coyote Creek station reflect the higher apparent complexing capacity than is found in the more northern reaches of Lower South San Francisco Bay. The higher apparent complexing capacity of waters at the Coyote Creek station can be attributed in part to higher concentration of suspended solids and total organic carbon. The 3-station geometric mean, which includes the Coyote Creek station, is used here to define the upper end of WER values used to develop the range of SSOs.

Table 5-2
Range of Water Effects Ratio Values

Option	WER Corresponding	Individual Station Geometric Means with Individual Station Minimum and Maximum Values
2-station pooled data (geometric mean n=40)	2.77	Dumbarton South = 2.87 (2.47 to 5.24) Dumbarton North = 2.67 (2.50 to 4.45)
3-station pooled data (geometric mean n=60)	3.00	Dumbarton South = 2.87  Dumbarton North = 2.67  Coyote Creek = 3.53 (2.90 to 5.65)

The values from Table 5-1 and 5-2 have been used to develop a range of values for SSOs by multiplying the range of ERCs by the range of WERs. The possible values for SSOs are listed in Table 5-3. These values range from a maximum of 16.2µg/L (Resident/Surrogate 90% ERC multiplied by 3-station WER) to a minimum of 1.4µg/L (Resident 99% ERC multiplied by 2-station WER). The range of possible SSOs exceeds a manageable range of SSOs to be considered for recommendation and would be more useful to the stakeholders if narrowed based on best professional judgement. In the following section the technical project team selects values believed to be the best estimates available for developing a recommended SSO for dissolved copper. The range of values and the algorithm enables stakeholders to develop additional alternative recommendations based on their own evaluation of the technical data.

Table 5-3

Range of Possible Values Using Various SSO Algorithm Options

Toxicity Database / %		2-Station WER	3-Station WER	
Community Taxa Protected	μg/L	2.77	3.00	
National/No Plant 90%	5.1	13.8	15.3	
National / No Plant 95 %	2.6	7.2	7.8	
National / No Plants 99 %	0.6	1.7	1.8	
EPA "WER Cookbook" 90%	4.0	10.8	12.0	
EPA "WER Cookbook" 95%	2.2	6.1	6.6	
EPA "WER Cookbook" 99%	0.6	1.6	1.8	
Resident & Surrogate 90%	5.4	15.0	16.2	
Resident & Surrogate 95%	3.1	8.6	9.3	
Resident & Surrogate 99%	0.9	2.5	2.7	
Resident 90%	4.2	11.6	12.6	
Resident 95%	2.2	6.1	6.6	
Resident 99 %	0.5	1.4	1.5	

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### 5.4.2 SSO Recommendation for Dissolved Copper

When numerical calculations involve multiple steps, there is always a concern about the propagation of error and the magnitude of the uncertainty associated with the output. The calculation of the proposed SSO values based on the AERAP methodology involved four steps, and the uncertainty associated with the proposed copper SSO values was evaluated by examining the effects of selecting different values for the input at each step in the calculation. Using this approach, referred to as combinatorial analysis (Morgan and Henrion, 1998), the calculation at each step in the development of an SSO value was made using both high and low estimates from the range of possible input. This produced a scenario tree (Figure 5-1) in which each node represents an uncertain quantity, and each branch from that node represents one of the possible SSO values.

The four steps in the calculation of the SSO values were:

- 1. Selection of an appropriate copper toxicity database. Four different databases that include the acute responses (LC50) of selected organisms to copper exposures were considered (see Section 5.4.1).
- 2. The selected toxicity databases provided values to which a logistic equation was fit to represent the relationship between ambient concentrations of copper and effect level [i.e., cumulative percentage of species affected (see Figure 4-5)]. The points on the curve generated in this part of the analysis give different Environmental Risk Concentrations (ERCs).
- 3. The ERCs are calculated using acute response data. However, the primary interest is in selecting an environmental criterion (SSO) that is protective of chronic exposures. This is accomplished by multiplying the calculated ERCs by an Acute-to-Chronic Ratio (ACR).
- 4. The candidate SSO values are calculated in the final step of the analysis by multiplying the chronic-response criterion by the Water Effects Ratio (WER), described in Section 4.3.5, to account for site specific conditions.

The combinatorial analysis considered the effects of uncertainty introduced at each of these steps in the analysis:

**Selection of the Appropriate Toxicity Database** - Four different databases consisting of between 13 to 28 toxicity test results were considered in the calculation of the ERC. Initial analyses (Table 5-1) had shown the use of the Resident toxicity database resulted in the lowest ERC and the Resident/Surrogate toxicity database resulted in the highest ERC. Both these databases as well as the National database were used in the uncertainty calculations.

**Sensitivity of the Logistic Model to the Variability Associated with Measured Toxicity Values -** The toxicity databased provide alternative sets of values to which a logistic equation was fit to represent the relationship between ambient concentrations of copper and effect level [i.e., cumulative percentage of species affected (see Figure 4-5)]. To evaluate the effect of variability in individual toxicity values on the calculated ERC values, three sets of sensitivity analyses were conducted for the three selected toxicity databases. First, the lowest values in the

data set were perturbed. ERC values were calculated after increasing or decreasing the lowest value in the data set by factors of 0.1, 0.2, and 0.5. Then these calculations were repeated while perturbing the median values and then the highest values in the data sets by the same factors. For each perturbation, the value of the ERC protective of 95% (ERC5%), 99% (ERC1%) and 90% (ERC10%) of the species affected was calculated.

The results of these sensitivity analyses performed on the Resident, National, and the Resident/Surrogate databases are presented in Tables 5-4, 5-5 and 5-6, respectively. Focusing on the values in the ERC5% column of Table 5-4, for example, it can be seen that the calculated value of the ERC5% is 8.2 ug/l. That is the value that corresponds to the unperturbed values in the National database. In general it can be seen that the calculated ERC values are not especially sensitive to large perturbations in the toxicity values. The lowest ERC5% value (5.3 ug/l) was obtained when the lowest value in the Resident Species database was reduced by a factor of two (the actual value of 9.6 ug/l in the Resident Species database was replaced by a value of 4.8 ug/l). The highest value for the ERC5% (10.0 ug/l) was obtained by replacing the highest value in the Resident/Surrogate database (540 ug/l) by a value of 270 ug/l. Combining the results from both sets of perturbation analyses gives a range of 5.3 – 10.0 ug/l. These values are shown in the initial node in the scenario tree (Figure 5-1) and represent the uncertainty associated with the first two steps in the calculation of the candidate SSO value.

**Variability in Acute to Chronic Ratios (ACRs) -** At the next step in the calculation, two values were used in the conversion of the acute to chronic toxicity values. Each acute value was divided by either 3.127, the currently accepted ACR and 2.388, the saltwater ACR value that is currently under review by the U.S. EPA.

**Alternative Water Effects Ratio (WER) Values -** In the final step of the calculation both the 2- and 3- station average WER values (2.77 and 3.0) were used to calculate SSO values.

The final range of ERC5% values from the combinatorial analysis was 4.7 to 12.6 ug/l. The median value was 8.4 ug/l. Based on these results the recommended range of SSO values for dissolved copper is 5 - 12 ug/l.

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Table 5-4 Sensitivity of ERC $_{x\%}$  to Changes in Toxicity Values: National Database All Values are Dissolved Copper in  $\mu g/L$ 

Lowest Values in the Data Set		ERC 5%	ERC 1%	ERC <sub>90%</sub>
L <sub>0.5 Nat'l</sub>	4.8	7.4	1.6	14.8
L <sub>0.8</sub>	7.7	8.0	1.8	15.7
$L_{0.9}$	8.6	8.1	1.8	15.9
$L_{Nat'I}$	9.6	8.2	1.9	16.1
L <sub>1.1</sub>	10.6	8.3	1.9	16.2
L <sub>1.2</sub>	11.5	8.4	1.9	16.4
L <sub>1.5</sub>	14.4	8.6	2.0	16.8
Median Values	s in the Data Set			
$M_{0.5}$	56.3	8.0	1.8	15.6
$M_{0.8}$	90.0	8.2	1.8	16.0
$M_{0.9}$	101.2	8.2	1.9	16.0
M	112.5	8.2	1.9	16.1
$M_{1.1}$	123.8	8.2	1.9	16.1
$M_{1.2}$	135.0	8.3	1.9	16.2
$M_{1.5}$	168.8	8.3	1.9	16.2
Highest Values	s in the Data Set			
H <sub>0.5</sub>	3462.5	9.0	2.2	17.0
$H_{0.8}$	5540.0	8.5	2.0	16.4
H <sub>0.9</sub>	6232.5	8.3	1.9	16.2
Н	6925.0	8.2	1.9	16.1
H <sub>1.1</sub>	7617.5	8.1	1.8	15.9
H <sub>1.2</sub>	8310.0	8.0	1.8	15.8
H <sub>1.5</sub>	10,387.5	7.8	1.7	15.5

Table 5-5
Sensitivity of ERC<sub>x%</sub> to Changes in Toxicity Values:
Resident/Surrogate Database
All Values are Dissolved Copper in μg/L

Lowest Values in the Data Set		ERC <sub>5%</sub>	ERC 1%	ERC 90%
L <sub>0.5</sub>	4.8	8.0	2.1	14.8
L <sub>0.8</sub>	7.7	9.1	2.5	16.2
L <sub>0.9</sub>	8.6	9.3	2.6	16.5
L	9.6	9.6	2.7	16.9
L <sub>1.1</sub>	10.6	9.8	3.0	17.2
L <sub>1.2</sub>	11.5	9.9	2.9	17.4
L <sub>1.5</sub>	14.4	10.4	3.1	18.1
Median Values in	the Data Set			
$M_{0.5}$	56.3	9.2	2.6	16.3
$M_{0.8}$	90.0	9.5	2.7	16.7
$M_{0.9}$	101.2	9.5	2.7	16.8
M	112.5	9.6	2.7	16.9
$M_{1.1}$	123.8	9.6	2.7	16.9
$M_{1.2}$	135.0	9.6	2.7	17.0
$M_{1.5}$	168.8	9.6	2.7	17.0
Highest Values in	the Data Set			
H <sub>0.5</sub>	270.0	10.0	3.0	17.4
H <sub>0.8</sub>	432.0	9.7	2.8	17.1
H <sub>0.9</sub>	486.0	9.6	2.8	17.0
Н	540.0	9.6	2.7	16.9
H <sub>1.1</sub>	594.0	9.4	2.7	16.8
H <sub>1.2</sub>	648.0	9.4	2.6	16.7
H <sub>1.5</sub>	810.0	9.1	2.5	16.4

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Table 5-6
Sensitivity of ERC<sub>x%</sub> to Changes in Toxicity Values:
Resident Species Database
All Values are Dissolved Copper in μg/L

Lowest Values in the Data Set		ERC 5%	ERC 1%	ERC 90%
L <sub>0.5</sub>	4.8	5.3	1.1	10.7
L <sub>0.8</sub>	7.7	6.3	1.5	12.4
L <sub>0.9</sub>	8.6	6.6	1.6	12.8
L	9.6	6.9	1.6	13.2
L <sub>1.1</sub>	10.6	7.1	1.7	13.6
L <sub>1.2</sub>	11.5	7.3	1.8	13.9
L <sub>1.5</sub>	14.4	7.9	2.0	14.7
Median Values in th	ne Data Set			
$M_{0.5}$	58.5	6.5	1.6	12.4
$M_{0.8}$	93.6	6.8	1.6	13.0
$M_{0.9}$	105.3	6.8	1.6	13.1
M	117.0	6.9	1.6	13.2
$M_{1.1}$	128.7	6.9	1.6	13.3
$M_{1.2}$	140.4	6.9	1.6	13.3
M <sub>1.5</sub>	175.5	6.9	1.6	13.4
Highest Values in the	he Data Set			
H <sub>0.5</sub>	236.7	7.5	1.9	14.0
H <sub>0.8</sub>	378.7	7.1	1.8	13.5
H <sub>0.9</sub>	426.1	7.0	1.7	13.3
Н	473.4	6.9	1.6	13.2
H <sub>1.1</sub>	520.7	6.8	1.6	13.0
H <sub>1.2</sub>	568.1	6.7	1.6	12.9
H <sub>1.5</sub>	710.1	6.4	1.4	12.6

### 5.4.3 Range of Values To Develop Site-Specific Objectives for Dissolved Nickel

The AERAP was not used as an assessment tool for nickel because its addition would not have added any additional value to the results obtained by the City of San Jose during their "Recalculation of the National Marine Water Quality Criterion and Developmento of a Site-Specific Nickel Criterion" study. This study used the procedures described in the WER Cookbook to update the National data set and recalculate a new national water quality criterion for nickel that was based on site-specific species composition. Since this procedure had already been used by the City to calculate several potential site-specific water quality objectives for the South Bay, the technical project team used the information provided by the City to develop a range of SSO values for dissolved nickel and to develop a recommended SSO.

The dissolved nickel values are developed by taking the Final Acute Values (FAV) developed from toxicity tests measuring the sensitivity of organisms to dissolved nickel and dividing that value by an acute to chronic ratio (ACR). For example the existing national criteria is based on the following calculation:

Formula: FAV / ACR = Criteria Continuous Concentration (CCC)

 $149.2 \mu g/L / 17.99 = 8.29 \mu g/L$  (National CCC)

The range of values listed in Table 5-7 for dissolved nickel are derived from the use of an updated national data set and a resident species data set that were developed as part of a study conducted by the City of San Jose (Watson, et al 1996, 1999). The values listed in Table 5-7 were developed as part of the study, *Acute and Chronic Nickel Toxicity: Development of a Site-Specific Acute-to-Chronic Ratio for South San Francisco Bay* (City of San Jose 1998). The study was also reviewed by Dr. Thursby U.S. EPA National Health and Environmental Effects Research Laboratory to evaluate whether or not study results could be used to develop site-specific objectives. Dr. Thursby made recommendations for some minor changes and clarifications, but accepted the technical conclusions of the study.

#### 5.4.4 Recommended Site-Specific Objective for Dissolved Nickel

**Step 1:** The acute sensitivity results of toxicity tests using resident and west coast species are added to the national data-set. A recalculation of the National Final Acute Value (FAV) using the Lower South San Francisco Bay resident species yields a site-specific FAV of 124.8 μg/L.

**Step 2:** The quotient of the acute and chronic response of each resident and west coast species is calculated. This quotient is called the acute-to-chronic ratio (ACR). Each of these ACR values is included with the ACR values in the national data-set and the geometric mean of either all of them, or a portion, is calculated. This data-set includes 4 marine and 2 freshwater ACR values. The geometric mean of all 6 of these ACR values (freshwater and marine) is calculated to be 10.50. This value is called the Final Acute-to-Chronic Ratio Combined (FACR-comb). The geometric mean of only the 4 marine ACR is calculated to be 5.959. This value is called the Final Acute-to-Chronic Ratio Marine (FACR-mar).

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**Step 3:** To develop all possible SSO recommendation combinations the FAVs (Updated National and Resident) are divided by the FACR-combined fresh/marine or FACR-marine to produce a Final Chronic Values (FCV). The range of values for the Final Acute Values (FAV) calculated from the toxicity dataset options and the possible Acute to Chronic Ratios (ACRs) have been arranged in Table 5-7 to develop the range of possible SSO recommendations for dissolved nickel. The possible FCVs are displayed in the cells of Table 5-7. These values that represent the range of possible SSO recommendation for dissolved nickel. Multiplying the various combinations of FAVs with the ACRs produces a range of recommended SSOs with a maximum of 24.4  $\mu$ g/L (Updated National divided by the Marine ACR) and a minimum of 11.89  $\mu$ g/L (Resident Species divided by the Combined Fresh / Marine ACR).

Table 5-7
Range of Values for Total and Dissolved Nickel SSOs

	FAV Toxicity Datasets		
FACRs	Updated National 145.5 μg/L	Resident Species 124.8 µg/L	
Combined Fresh/Marine ACR	13.9 μg/L (Total)	11.89 μg/L (Total)	
10.50	13.6 μg/L (Dissolved) <sup>*</sup>	11.6 μg/L (Dissolved) <sup>*</sup>	
Marine ACR	24.42 μg/L (Total)	20.94 μg/L (Total)	
5.95	23.9 μg/L (Dissolved) <sup>*</sup>	20.5 μg/L (Dissolved) <sup>*</sup>	

<sup>\*</sup>Dissolved concentrations based on a Total to Dissolved conversion factor of 0.98 (Dan Watson. Personal Communication 1999. City of San Jose)

Completing Steps one through three results in a recommended range of site-specific objectives. The project team offers this recommended range as a starting point for discussion for the stakeholder group. There is less supplemental information to use in stakeholder consideration of the recommended range of SSOs for dissolved nickel. However, the limited toxicity information included as part of this report suggests that resident species toxicity sensitivity are below the recommended range and existing ambient concentrations. The steps used in the development of an SSO recommendation for dissolved nickel can be used by the Initiative to focus discussions and to build consensus on an Initiative recommendation for which the rationale can be explicitly documented.

Based on the information presented, there is no evidence that the Lower South San Francisco Bay is being impaired by nickel. This conclusion is based on the following:

- Ambient water column concentrations of dissolved nickel in the Lower South San Francisco Bay between 1989 and 1999 averaged 4.2 μg/L;
- Ambient sediment nickel concentrations in the Lower South San Francisco Bay averaged 92 mg/kg (dry wt) between 1994 and 1997 were not greater than those found in the rest of the Bay and lower than those found in the relatively pristine Tomales Bay;

- Any instances of observed ambient toxicity in the Lower South San Francisco Bay could not be attributed to toxic concentrations of nickel; and
- A recalculation of the National and Site-Specific water quality objectives for nickel indicated that dissolved nickel concentrations ranging from 11.6 to 13.6 μg/L in the Lower South San Francisco Bay would be protective of Beneficial Uses.

### 5.5 Summary and Recommendations Relative to 303(d) Listing

The current state of scientific knowledge is sufficient to establish a SSO for dissolved copper and nickel. An SSO for dissolved copper in the range of 5.0 to 12.0 µg/L is scientifically defensible. An SSO for dissolved nickel in the range of 11.6 to 20.5 is also scientifically defensible. An important, but not essential input to a final SSO would be to conduct further special studies for the uncertainties identified in this report. For example key uncertainties are phytoplankton uptake and toxicity of dissolved copper, and additional knowledge on copper cycling in the bay. The TMDL Work Group (TWG) should begin the process of narrowing the ranges for potential SSOs with the goal of recommending a final numeric value for the Regional Board to consider. The Regional Board will need to develop the necessary legal and policy bases to accompany this technical information for a final recommendation.

The analyses presented in this report indicate that even if an SSO is established at the low end of the respective justifiable ranges for dissolved copper and nickel, such SSOs would be attained in the main water mass of Lower South San Francisco Bay. Based on the above assessment findings and recommendations it is clear that a significant body of technical evidence has been compiled along with an assessment of beneficial uses that supports the recommendation that the 303 (d) should be updated to delist copper and nickel as stressors for the Lower South Bay.

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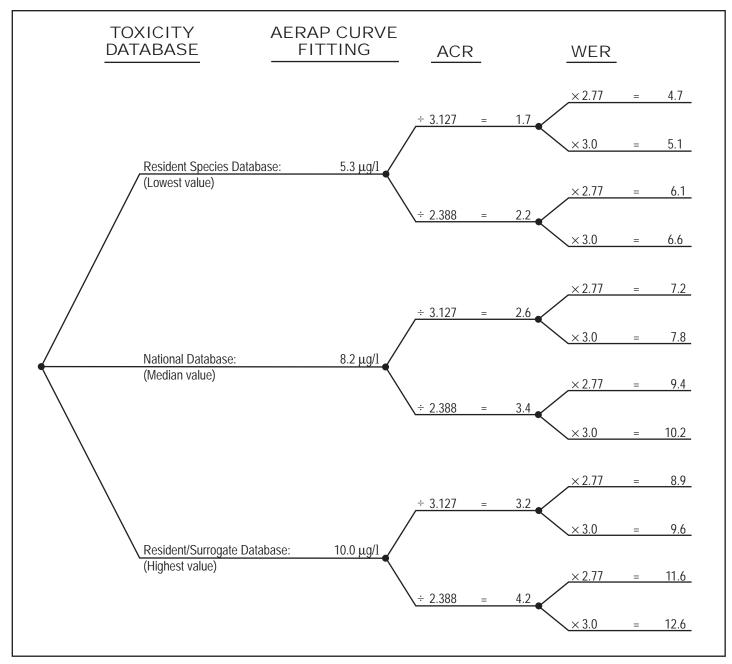


Figure 5-1. Scenario tree from combinatorial analysis of uncertainty in copper SSO calculation.



### 6.0 RISK MANAGEMENT DECISIONS

On May 12, 1999, the Project Management Group of the WMI TMDL Workgroup (TWG) decided that the Impairment Assessment Report would be more useful to the TWG if it contained an outline of some of the key risk management (i.e., policy) decisions the TWG needs to make in light of the recommendations in Chapter 5 of the report. What follows is an initial draft outline of Chapter 6. This outline will be further developed and distributed to TWG members prior to the TWG's scheduled meeting on June 15, 1999.

6.1 Risk Management Judgments upon which the Report's Recommendations Are Based

The recommendations in Chapter 5 are based in part on assumptions and determinations which required judgment by the technical consultants. TWG members are asked to raise any important concerns they may have with these judgments by June 2, 1999, in their initial comments on the report. This section will then be further developed as appropriate to identify and possibly outline considerations relevant to members' concerns with the assumptions and logic of the report.

The following questions illustrate the types of issues the TWG may wish to consider in reviewing the judgments reflected in the report:

- What **percent of taxa** should be protected? (The EPA water quality criterion guidelines require that water quality standards must protect 95% of the species present in the aquatic system, but other options are explicitly discussed in the text.)
- Does the TWG agree that a **weight of evidence** approach should be used in the assessment? (This approach is recommended by EPA guidance and discussed in the text.)
- Is an appropriate **level of conservatism/margin of safety** used in calculating the water quality objective? (Aspects of this issue are discussed in several places in the text.)
- 6.2 Risk Management Decisions Needed if the Report's Proposed Approach is Accepted

Assuming the basic analysis and recommendations by the technical consultants are acceptable to the TWG, the TWG will need to decide how to proceed. Since the South San Francisco Bay is identified on California's list of impaired waters under Section 303(d) of the federal Clean Water Act, a TMDL must be developed, or, if the water is no longer impaired or was erroneously listed, copper and nickel should be removed from the list for the South Bay.

The first step in many TMDLs is an assessment of whether designated beneficial uses are being protected and whether any applicable water quality criteria are being attained and, if they are not, the specific objectives that must be achieved to protect the beneficial uses. The result of the assessment could be a finding that uses are not being attained. In such a case, the objectives developed in the assessment are generally used to support development of a wasteload allocation and an implementation plan which must be approved by U.S. EPA as part of the TMDL.

If, on the other hand, the result of the assessment is a finding that uses are (or most likely are) being protected and are not threatened (i.e., are not likely to become impaired within the next two years), the waterbody is removed from the Section 303(d) list of impaired waters. While extremely rare due to costs and other priorities, a State TMDL may still be done at some point for information or planning purposes. However, federal law does not establish deadlines or require that such a TMDL be submitted to EPA for approval.

Whether or not a TMDL is required or completed, the assessment may also lead to establishment of new and/or modified water quality criteria or site specific objectives as part of the State's applicable water quality standards. These also must be approved by EPA.

# Issue I: Are the data of sufficient quality and quantity to make a decision on appropriate water quality objectives (SSOs) and attainment/impairment status now?

The technical consultants recommend that certain additional studies be undertaken to reduce uncertainties. Some level of uncertainty is a constant in water quality decisions and the TWG could decide that enough information and analysis exist to support selection of objectives and determine attainment/impairment status now, without additional study. The following factors might be weighed in making this risk management decision:

- Adaptive management may be an appropriate approach. Section 303(d) lists are revisited every 2 years and new information can be considered.
- **Benchmarking** may help guide the TWG's decision. Nationally, water quality objectives are usually established with less data and analysis than is currently available on the South San Francisco Bay.
- Environmental risk must be considered. Considering all the data and given the trends in copper and nickel concentrations in the South Bay, is there reason to believe that environmental harm could result from establishing the recommended objectives and removing the South Bay from the Section 303(d) list now? If so, is the harm likely to be significant and/or irreversible?
- **Time and resources** needed to conduct the studies may be weighed against their likely utility. If the studies can be done quickly and cheaply, and they are highly likely to resolve remaining uncertainties, this may be a relatively easy decision. If not, are there other, perhaps more important water quality issues that need to be addressed with the limited resources available?

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## Issue II: If the data are sufficient to establish SSOs and determine that uses are protected, what are the appropriate SSOs?

Chapter 5 suggests a range of SSO values that could be recommended by the TWG to the Regional Board. What specific recommendations would the TWG make to the Board based on the considerations described in Chapter 5? Would it be appropriate to recommend a range to the Board?

Issue III: Assuming the TWG decides to recommend SSOs and a finding that uses are adequately protected, should it also recommend performing the studies suggested by the technical consultants? If so, would this be a high, medium or low priority?

The recommended studies may be desirable, even if not necessary for a decision at this time. Given the costs, timing, and likely utility of the studies, would the TWG recommend that they be undertaken? If so, would the TWG recommend that they be undertaken on an urgent basis, within some specified time, or at some future (unspecified) time, and with what funding mechanism? Would the TWG recommend that other specific water quality activities (e.g., work on other pollutants for which more certainty exists of the extent or severity of impairment) be undertaken instead of the recommended studies or that these other activities receive higher or lower priority than the recommended studies?

### 6.3 Next Steps

Sections 6.1 and 6.2 are intended to stimulate consideration of certain key issues. They may provide a framework for beginning to evaluate TWG recommendations, but are not intended to serve as an outline of all risk management issues the TWG may need to consider. TWG members themselves must identify the key issues of concern to them.



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